Crystal Structure and Triboluminescence 2. 9-Anthracenecarboxylic Acid and Its Esters

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Triboluminescence activity is usually assumed to be a consequence of crystal dissymmetry; however, the multitude of reports of centrosymmetric triboluminescent materials cast doubt on that assumption. We examine here the connection between triboluminescence and crystal symmetry without prejudice, by synthesizing 12 esters of 9-anthracenecarboxylic acid and correlating their triboluminescence activity and that of the acid with crystal structure, purity, and photoluminescence. In this series, a noncentrosymmetric crystal structure is necessary but not sufficient for triboluminescence in relatively pure materials; impurities are necessary for triboluminescence activity in all centrosymmetric and one noncentrosymmetric materials. Crystallization motif and other structure factors were only weakly correlated with triboluminescence. The results provide evidence in support of a charge separation and recombination mechanism for the excitation of the triboluminescence.

Introduction

Triboluminescence, the emission of light by solids when they are mechanically deformed or fractured, has been observed for hundreds of years but is still poorly understood.[1,2] In 1922, Longchambon published the first triboluminescence spectrum, that of sucrose.[3] Because the sucrose emission spectrum is identical with that of dinitrogen excited in an electrical discharge, and its intensity is sensitive to atmospheric pressure, Longchambon concluded that a discharge occurs between rapidly separated, charged fragments. He also noted that noncentrosymmetric crystals are more likely to be triboluminescent than centrosymmetric crystals[4] but pointed out that there was no evidence that the piezoelectricity of noncentrosymmetric crystals causes the charge separation. There is now general agreement that triboluminescence consisting of a dinitrogen discharge occurs as Longchambon proposed.[2,3]

Over the years, the strong correlation of noncentrosymmetric crystal structure with triboluminescence has led most observers to conclude that the piezoelectric properties of noncentrosymmetric crystals are always the source of triboluminescence. Yet there are many exceptions. Using literature crystal structures and reports of triboluminescence, plus their own observations of triboluminescence activity, Chandra and Zink[5,6] reported on the relationship between triboluminescence and crystal symmetry for 58 sulfates and nitrates: triboluminescence was observed for 20 centrosymmetric materials in addition to 26 noncentrosymmetric materials. Even centrosymmetric undoped alkali halides are triboluminescent, producing the dinitrogen discharge spectrum indicative of charge separation when fractured.[7,8] All sugars have sufficient dissymmetry to separate charge, but not all are triboluminescent.[9] Likewise, while many glassy polymers are triboluminescent,[10] glassy sucrose is not, even though its chiral molecules make it noncentrosymmetric.[11] Thus, despite the general acceptance of piezoelectricity as the source of triboluminescence, a noncentrosymmetric structure appears to be neither necessary nor sufficient for triboluminescence.

Impurities can influence triboluminescence activity. Saccharin has been shown to owe its triboluminescence completely to impurities.[12] Doped and irradiated alkali halides emit light characteristic of recombination of defects when they are deformed instead of the weak dinitrogen discharge emission seen upon fracture of pure materials.[13,14] Crystal disorder too may be important but does not seem to be a common source of activity.[15,16]

Photoluminescent materials have triboluminescence spectra which are nearly identical with their solid-state

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photoluminescence, usually with no spectral evidence of an electrical discharge.[17] One notable exception is uranyl nitrate hexahydrate, whose triboluminescence includes a reproducible trace (0.5%) of dinitrogen emission with the dominant photoluminescence.[18,19] Since this was the only photoluminescent material that Longchambon studied, he concluded that the fluorescence was excited by the discharge, which he believed to be the primary event. It should be noted that the presence of a dinitrogen discharge spectrum with photoluminescence can be misleading, since discharge between the material and the grinder or the stationary and moving parts of the grinder is also possible; such spurious emission is unlikely to be reproducible.[17] Casual observation indicates that the most brightly triboluminescent materials are also photoluminescent, in part because almost all of their emission is detectable by eye (unlike the largely ultraviolet discharge emission of dinitrogen).

The high frequency of noncentrosymmetric crystal structures in triboluminescent photoluminescent materials (henceforth called tribophotoluminescent) also suggests a mechanism involving charge separation, despite the lack of spectral evidence. Our earlier work on photoluminescent 9-anthracenecarbinols is fairly typical:[20] the one nontriboluminescent carbinol was centrosymmetric; of the three triboluminescent compounds, two were noncentrosymmetric and one centrosymmetric. The triboluminescence spectra of the carbinols were almost identical with their solid-state photoluminescence spectra, with no reproducible dinitrogen emission. Others have observed similar correlations using tribophotoluminescent materials unrelated to each other structurally.[21,22]

The examination of triboluminescence (also known as mechanoluminescence[23] or fractoemission[24]) has thus far not been particularly systematic. Each factor affecting triboluminescence activity has been studied with a different set of materials, and observations on one crystalline compound have often been made on different samples in different laboratories, sometimes with different outcomes. As a consequence, we have been quite skeptical that the important factors are correctly identified, especially the necessity of noncentrosymmetric crystal structures for triboluminescence in reasonably pure compounds: too many exceptions have been documented. Still, we have no reason to doubt that triboluminescence is fundamentally an electrical phenomenon, mediated by pressure.

To provide a fresh and systematic examination of the connection between crystal structure and triboluminescence, we undertook a second study of anthracene derivatives, which usually crystallize well and are intensely photoluminescent. We synthesized a series of esters of 9-anthracenecarboxylic acid with varying steric and electronic characteristics whose triboluminescence was unknown when we began. Some of the esters are chiral, some racemic and some symmetric, and some have alkyl groups which might crystallize in a disordered manner. We report here the triboluminescence activity, the triboluminescence and photoluminescence spectra of the acid and 12 esters shown in Figure 1 and the crystal structures of all but two. We find that in this series a noncentrosymmetric crystal structure is necessary but not sufficient for triboluminescence and that impurities can enable triboluminescence activity for both centrosymmetric and noncentrosymmetric crystals.

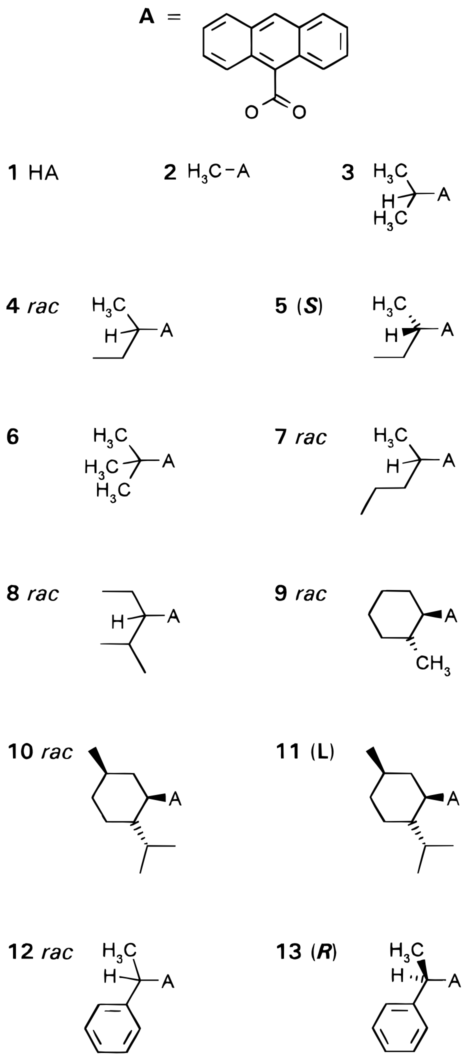

Figure 1. Acid and esters studied.

Experimental Section

Materials. The esters shown in Figure 1 were synthesized by a modification of the method of Parish and Stock.[25] 9-Anthracenecarboxylic acid was stirred with a 2- or 4-fold excess of trifluoroacetic anhydride in toluene until dissolved. A 2- or 4-fold excess of alcohol was added, and the mixture stirred for 30−100 min. The reaction mixture was warmed slightly in some cases. The ester solutions were extracted with base, dried over magnesium sulfate, and evaporated under

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heat and vacuum; the resulting solid or syrup was recrystallized. Exposure to light was minimized to prevent photochemical dimerization.[26] Several of the esters have been reported previously.[25−28] All reagents were purchased from the Aldrich Chemical Co., Inc., except for L-menthol (Fisher Scientific). Solvents were obtained from Fisher Scientific. Physical properties are given below.

9-Anthracenecarboxylic Acid (1). Recrystallization from ethanol or toluene gave yellow needles: mp 218−220 °C (Aldrich 220 °C (dec)); IR (KBr) 3000 (O−H), 1672 (C=O), 1250, 772 (aromatic C−H) cm^{-1}; ^{1}H NMR (acetone-d_6) δ 7.57 (m, 4), 8.17 (m, 4), 8.67 (s, 1, C$_{10}$H), OH not observed; ^{13}C NMR (acetone-d_6) δ 142.0 (2), 142.4 (2), 143.7 (2), 144.8, 145.4 (2), 145.6, 146.0, 148.0, 186.1; solid-state photoluminescence maximum 490 nm (excitation 396 nm).

Methyl 9-Anthracenecarboxylate (2). Recrystallization from ethanol gave yellow hexagonal tablets: mp 111−112 °C (lit. 112−113 °C[26]); IR (KBr) 2930 (C−H), 1714 (C=O), 1198, 1103, 1012 , 722 (aromatic C−H) cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 4.18 (s, 3, CH$_3$), 7.52 (m, 4), 8.03 (m, 4), 8.53 (s, 1, C$_{10}$H); no solid-state photoluminescence.

Isopropyl 9-Anthracenecarboxylate (3). Recrystallization from ethanol gave yellow needles or hexagonal plates: mp 96−100 °C (lit. 95 °C[26]); IR (KBr) 2979 (C−H), 1717 (C=O), 1215, 1001, 730 (aromatic C−H) cm^{-1}; ^{13}C NMR (CDCl$_3$) δ 22.1 ((CH$_3$)$_2$), 26.5, 124.8 (2), 125.4 (2), 126.8 (2), 128.2, 128.4 (C-9), 128.6 (2), 129.0, 131.0, 169.1 (C=O); solid-state photoluminescence maximum 436 nm (excitation 393 nm).

Racemic 1-Methylpropyl 9-Anthracenecarboxylate (4). Recrystallization from cyclohexane gave colorless hexagonal plates: mp 98−101 °C; IR (KBr) 1716 (C=O), 1218, 1001, 887, 729 (aromatic C−H); ^{1}H NMR (CDCl$_3$) δ 1.07 (t, 3, CH$_2$CH_3), 1.55 (d, 3, CHCH_3), 1.77, 1.85 (m, 2, diastereotopic CH$_2$), 5.46 (m, 1, CHO), 7.51 (m, 4), 8.03 (t, 4), 8.52 (s, 1, C$_{10}$H); solid-state photoluminescence weak, maximum 529 nm (excitation 408 nm). Anal. Calcd for C$_{19}$H$_{18}$O$_2$: C, 81.99; H, 6.52. Found: C, 81.85; H, 6.34.

(*S*)-1-Methylpropyl 9-Anthracenecarboxylate (5). Recrystallization from 1,4-dioxane gave pale yellow rectangular plates: mp 82−85 °C; IR (KBr) 2988 (C−H), 1707 (C=O), 1219, 1113, 998, 730 (aromatic C−H) cm^{-1}; ^{1}H NMR ((CD$_3$)$_2$CO) δ 1.04 (t, 3, CH$_2$CH_3), 1.51 (d, 3, CHCH_3), 1.75 (m, 2, CH$_2$), 5.36 (q, 1, CHCH$_3$), 7.61 (m, 4), 8.05 (m, 4), 8.65 (s, 1, C$_{10}$H); solid-state photoluminescence maximum 516 nm (excitation 413 nm); α_D^{20} +12.6 (c = 0.240, acetone).

***tert*-Butyl 9-Anthracenecarboxylate (6).** Recrystallization from ethanol gave rectangular needles: mp 157−160 °C (lit. 158 °C[25]); IR (KBr) 3060, 2990 (C−H), 1727 (C=O), 1254, 1160, 1015, 915, 747 (aromatic C−H) cm^{-1}; ^{13}C NMR (CDCl$_3$) δ 28.5 ((CH$_3$)$_3$), 82.9 (CO), 124.9 (2), 125.3 (2), 126.7 (2), 127.9, 128.4, 128.5 (2), 129.6 (C-9), 131.0, 169.0 (C=O); solid-state photoluminescence weak, maximum 506 nm (excitation 443 nm).

Racemic 1-Methylbutyl 9-Anthracenecarboxylate (7). Recrystallization from ethanol gave colorless cubes: mp 77−78 °C; IR (KBr) 2920 (C−H), 1706 (C=O), 1218, 742 (aromatic C−H) cm^{-1}; ^{1}H NMR ((CD$_3$)$_2$CO) δ 0.96 (t, 3, CH$_3$), 1.53 (d, 3, CHCH_3), 1.67 (m, CH$_2$CH$_2$), 5.49 (q, 1, CHCH$_3$), 7.56 (m, 4), 8.24 (m, 4), 8.60 (s, 1, C$_{10}$H); solid-state photoluminescence maximum 436 nm (excitation 405 nm).

Racemic 1-Ethyl-2-methylpropyl Anthracenecarboxylate (8). Recrystallization from toluene gave yellow chunks: mp 121−124 °C; IR (KBr) 2970 (C−H), 1715 (C=O), 1225, 1012, 899, 740 (aromatic CH) cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 1.03, 1.07 (dd, 6, diastereotopic (CH$_3$)$_2$), 1.10 (t, 3, CH$_3$), 1.86 (m, 2, CH$_2$), 2.20 (m, 1, CH(CH$_3$)$_2$), 5.29 (q, 1, CHO), 7.51 (m, 4), 8.05 (m, 4), 8.52 (s, 1, C$_{10}$H); solid-state photoluminescence maximum 473 nm (excitation 416 nm).

Racemic (*E*)-2-Methylcyclohexyl 9-Anthracenecarboxylate (9). Recrystallization from hexane gave yellow rectangular crystals: mp 136−138 °C; IR (KBr) 2945 (C−H), 1718 (C=O), 1234, 1020, 900, 745 (aromatic C−H) cm^{-1}; ^{1}H NMR ((CD$_3$)$_2$CO) δ 1.09 (d, 3, CH$_3$), 1.1−1.8 (m, CH$_2$'s), 2.03 (m, 1, CHCH$_3$), 4.11 (m, 1, OCH), 7.60 (m, 4), 8.10 (m, 4), 8.68 (s, 1, C$_{10}$H); ^{13}C NMR ((CD$_3$)$_2$CO) δ 16.1, 35.2, 41.6, 42.0, 50.4, 54.0, 97.2 (CO), 141.8, 142.5, 143.8, 144.9, 145.6, 148.2, 185.7 (C=O); solid-state photoluminescence maximum 511 nm (excitation 404 nm).

***rel*-(1*R*, 2*S*, 5*R*)-Menthyl 9-Anthracenecarboxylate (10).** Recrystallization of racemic ester from ethanol gave glittery colorless cubes: mp 187−188 °C; IR (KBr) 2957 (C−H), 1706 (C=O), 1225, 733 (aromatic C−H) cm^{-1}; ^{13}C NMR (CDCl$_3$) δ 15.9, 20.8, 22.1, 23.0, 25.9, 31.7, 34.2, 41.0, 46.9, 76.3 (CO), 124.8 (2), 125.4 (2), 126.8 (2), 128.0, 128.6 (2), 128.7, 131.0, 169.4 (C=O); solid-state photoluminescence maximum 425 nm (excitation 398 nm).

(1*R*, 2*S*, 5*R*)-Menthyl 9-Anthracenecarboxylate (11) (L-Menthyl 9-Anthracenecarboxylate). Recrystallization from cyclohexane gave colorless, odorless needles: mp 207−208 °C; IR (KBr) 2940 (C−H), 1700 (C=O), 1214, 1003, 725 (aromatic C−H) cm^{-1}; ^{1}H NMR ((CD$_3$)$_2$CO) δ 0.88 (d, 3, CH$_3$), 1.01 (d, 3, CH$_3$), 1.05 (d, 3, CH$_3$), 1.26 (dt, 1, axial CH), 1.34 (t, 1, axial CH), 1.51 (tt, 1, axial CH), 1.73 (m, 1, CHCH$_3$), 1.78 (d, 1, axial CH), 2.10 (m, 1, CH(CH$_3$)$_2$), 2.56 (d, 1, axial CH), 2.83 (s, 1, equatorial CH), 2.87 (s, 1, equatorial CH), 5.27 (dt, 1, OCH), 7.60 (m, 4, arom CH), 8.05 (d, 2, arom CH), 8.16 (d, 2, arom CH); ^{13}C NMR ((CD$_3$)$_2$CO) δ 16.4, 21.0, 22.4, 23.9, 26.8, 32.4, 35.0, 41.8, 47.9, 76.8 (CO), 125.6 (2), 126.5 (2), 127.8 (2), 128.8, 129.6 (2), 129.6, 130.0, 132.0, 169.5 (C=O); α_D^{20} −28 (c = 0.0028, C$_2$H$_5$OH); solid-state photoluminescence maximum 425 nm (excitation 400 nm); triboluminescence maximum 455 nm (459 for later run, 440 for smaller, less pure crystals). Anal. Calcd for C$_{25}$H$_{28}$O$_2$: C, 83.29; H, 7.83. Found: C, 83.52; H, 7.81.

Racemic 1-Phenylethyl 9-Anthracenecarboxylate (12). Recrystallization from cyclohexane gave pale yellow chunks: mp 95−100 °C; IR (KBr) 3025 (C−H), 1716 (C=O), 1220, 1000, 715 (aromatic C−H) cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 1.82 (d, 3, CH$_3$), 6.50 (q, 1, CH), 7.3−7.6 (m, 9, aromatic H), 7.85−8.05 (m, 4, anthracene CH), 8.51 (s, 1, C$_{10}$H); ^{13}C NMR (CDCl$_3$) δ 22.4 (CH$_3$), 74.0 (CH), 125.0 (2), 125.4 (2), 126.6 (2), 126.8 (2), 128.1, 128.2, 128.4, 128.5 (2), 128.6 (2), 129.1, 131.0, 141.3, 168.9 (C=O); solid-state photoluminescence maximum 514 nm (excitation 404 nm); solution photoluminescence maximum 453 nm (toluene), 470 nm (methanol).

(*R*)-1-Phenylethyl 9-Anthracenecarboxylate (13). Recrystallization from ethanol gave yellow needles: mp 50−53 °C; IR (KBr) 1715 (C=O), 1200, 990, 885, 727, 689 (aromatic C−H) cm^{-1}; ^{1}H NMR ((CD$_3$)$_2$CO) δ 1.81 (d, 3, CH$_3$), 6.50 (q, 1, OCH), 7.34−7.60 (m, 9), 7.93 (m, 2, phenyl CH), 8.13 (m, 2, phenyl CH), 8.70 (s, 1, C$_{10}$H); ^{13}C NMR ((CD$_3$)$_2$CO) δ 22.5 (1, CH$_3$), 74.8 (CH), 125.6 (2), 126.5 (2), 127.5 (2), 127.8 (2), 129.0, 129.0, 129.4, 129.4 (2), 129.5 (2), 129.9, 132.0, 142.5, 169.1 (C=O); solid-state photoluminescence maximum 465 nm (excitation 389 nm); α_D^{20} +73 (c = 0.0050, C$_2$H$_5$OH). Under standard conditions of preparation, some racemization occurred; this was avoided by evaporating the solution at room temperature.

NMR spectra were taken on a JEOL FX-90Q, a Varian XL-300, or a Bruker WM-300; carbon-13 spectra were acquired with repetition rates sufficient for complete relaxation of protonated carbons but not unprotonated carbons. Infrared spectra were taken on a Perkin-Elmer 1400, 735, or 1621 or a Nicolet 740.

X-ray Crystallographic Studies. Crystals of sufficient lateral dimensions were obtained by room-temperature evaporation of solutions in the solvents listed in Table 2. **2**, **7**−**10**, and **12** crystallized as cubes or irregular chunks; the others were examined as needles or cut from needles.

Crystal, data collection and refinement parameters are given in Table 1. Suitable crystals for single-crystal X-ray diffraction were selected and mounted with epoxy cement on a thin glass fiber. The unit-cell parameters were obtained by the least-squares refinement of the angular settings of 24 reflections (20° ≤ 2θ ≤ 25°).

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Table 1. Crystallographic Data for 3, 4, and 6−12

	3	**4**	**6**	**7**	**8**	**9**	**10**	**11**	**12**
(a) Crystal Parameters									
formula	$C_{18}H_{16}O_2$	$C_{19}H_{18}O_2$	$C_{19}H_{18}O_2$	$C_{20}H_{20}O_2$	$C_{21}H_{22}O_2$	$C_{22}H_{22}O_2$	$C_{25}H_{28}O_2$	$C_{25}H_{28}O_2$	$C_{23}H_{18}O_2$
formula weight	264.3	278.4	278.3	292.4	306.4	318.2	360.5	360.5	326.4
space group	*Pbca*	$P\bar{1}$	$P2_1/n$	*Pbca*	$P2_1/c$	$P\bar{1}$	$P2_1/n$	$P2_1$	$P\bar{1}$
a, Å	10.268(5)	7.773(2)	9.115(2)	35.31(2)	7.869(3)	8.796(2)	11.470(4)	9.972(4)	8.938(6)
b, Å	9.077(4)	10.577(3)	17.516(4)	10.239(5)	18.528(9)	9.850(2)	9.593(2)	9.632(3)	9.76(7)
c, Å	30.58(1)	11.148(3)	9.837(2)	9.089(4)	12.090(5)	11.442(3)	19.737(5)	11.499(4)	10.10(1)
α, deg		62.98(2)				103.16(2)			106.94(6)
β, deg		81.88(2)	100.26(4)		101.26(3)	99.52(2)	104.67(3)	104.79(3)	89.84(7)
γ, deg		68.88(2)				112.01(2)			90.29(6)
V, Å^3	2850(2)	761.4(3)	1545(2)	3286(3)	1729(1)	859.7(4)	2100.8(8)	1068.0(7)	846(1)
Z	8	2	4	8	4	2	4	2	2
cryst dimens, mm	0.4 × 0.4 × 0.4	0.3 × 0.4 × 0.4	0.2 × 0.2 × 0.3	0.2 × 0.3 × 0.3	0.3 × 0.4 × 0.4	0.3 × 0.4 × 0.4	0.3 × 0.4 × 0.4	0.1 × 0.4 × 0.4	0.2 × 0.2 × 0.3
D(calc), g cm^{-3}	1.23	1.21	1.196	1.18	1.18	1.22	1.14	1.12	1.28
μ(Mo Kα), cm^{-1}	0.74	0.72	0.76	0.70	0.69	0.72	0.70	0.65	0.81
temp, K	298	298	298	298	298	298	304	298	296
(b) Data Collection									
diffractometer	Siemens P4								
monochromator	graphite								
radiation	Mo Kα (λ = 0.710 73 Å)								
2θ scan range, deg	4.0−50.0	4.0−48.0	4.0−45.0	4.0−42.0	4.0−45.0	4.0−50.0	4.0−45.0	4.0−45.0	4.0−48.0
data collected (*h*,*k*,*l*)	+13, +11, +37	±9, ±12, +12	±9, +17, +9	+36, +11, +10	±9, +21, +14	±11, ±12, +14	+6, ±9, ±17	±11, +11, +13	±10, ±11, +11
rflns collected	2948	2642	1771	2150	2265	3213	3403	1529	2836
indpt obsvd rflns $F_o \geq n\sigma(F_o)$	1494 (n = 4)	1680 (n = 5)	1127 (n = 4)	1044 (n = 5)	1366 (n = 4)	1568 (n = 4)	1251 (n = 3)	1269 (n = 4)	1313 (n = 4)
(c) Refinement[a]									
$R(F)$, %	4.60	5.10	9.16	9.65	6.87	4.79	6.75	7.02	5.42
$R(wF)$, %	4.74	6.33	14.56	11.22	8.50	6.13	8.55	7.35	6.03
N_o/N_v	8.2	6.4	5.9	5.3	6.6	7.2	5.6	5.2	5.8

[a] Quantity minimized = $\sum w\Delta^2$; $R = \sum\Delta/\sum(F_o)$; $R(w) = \sum\Delta w^{1/2}/\sum(F_o w^{1/2})$, $\Delta = |(F_o - F_c)|$.

Table 2. Crystallographic Patterns and Tribo- and Photoluminescence of 9-Anthracenecarboxylic Acid and Its Esters

substituent		crystal symmetry[a]	structure motif	photoluminescence maximum (nm)	photoluminescence halfwidth (nm)	triboluminescence activity crude[b]	triboluminescence activity purified	triboluminescence recryst solvent
1	hydrogen	centro[c]	β	490	80	0	0	ethanol
2	methyl	centro[d]	SHB			0	0	ethanol
3	isopropyl	centro	HB	436	45	1	0	ethanol
4	1-methylpropyl	centro	FSHB	514	114[e]	1	0	ethanol
						1	0	cyclohexane
5	(*S*)−1-methylpropyl	noncentro		516	96	3	3	dioxane
						4	4	ethanol
6	*tert*-butyl	centro	SHB	506	87	0	0	ethanol
7	1-methylbutyl	centro	HB	436	45	1	0	ethanol
						2	0	cyclohexane
8	1-ethyl-2-methylpropyl	centro	FSHB	473	83	1	0	ethanol
9	(*E*)-2-methylcyclohexyl	centro	FSHB	512	90	0	0	hexane
10	racemic menthyl	centro	HB	425	40	0	0	ethanol
						3	0	cyclohexane
11	L-menthyl	noncentro	HB	425	45	5	4	toluene
12	racemic 1-phenylethyl	centro	FSHB	513	98	0	0	cyclohexane
13	(*R*)-1-phenylethyl	noncentro		465	81	1	0	ethanol

[a] centro = centrosymmetric, noncentro = noncentrosymmetric. [b] Activity scale: 1, just detectable; 3, equal to sucrose; 6, equal to triethylammonium tetrakis(dibenzoylmethide)europate. See Experimental Section for details. [c] **1** is reported to have space group $P\bar{1}$ in Heller's dissertation,[33] but $P1$ in the subsequent paper;[26] we have assumed that the thesis is correct. [d] The crystal structure of **2**[30] and the space group of an α polymorph of **3**[26,33] have been previously reported. [e] Emission of **4**, **5**, and **6** is weak.

The photographic data, unit-cell parameters and systematic absences in the diffraction data were consistent with $P1$ and $P\bar{1}$ for **4**, **9**, and **12**; $P2_1$ and $P2_1/m$ for **11**; and, uniquely, for $P2_1/n$ for **6** and **10**; $P2_1/c$ for **8**; and $Pbca$ for **3** and **7**. For the nonunique cases, the E statistics suggested a centrosymmetric space group for triclinic cases and a noncentrosymmetric space group for monoclinic cases. The space group choices were subsequently verified by chemically reasonable results of refinement. The structures were solved by direct methods, completed by subsequent difference Fourier syntheses and refined by full-matrix least-squares procedures. Three carbon atoms in **7**, C(18), C(19), and C(20), were disordered with a 50:50 distribution and were refined isotropically. All other non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were treated as idealized contributions.

All software and sources of the scattering factors are contained in several versions of the SHELXTL program libraries (G. Sheldrick, Siemens XRD, Madison, WI).

Triboluminescence and Photoluminescence. Samples were examined for triboluminescence after the first recrystallization, usually from ethanol, and then after 1−3 further crystallizations from the solvent indicated.

A crude scale of triboluminescence intensity was chosen to represent our ability to distinguish intensity visually. Samples were placed in test tubes, and crushed with glass rods. At least two people, after 15 min of dark adaptation, performed a "blind" comparison with two standard samples: triethylammonium tetrakis(dibenzoylmethide)europate (assigned intensity 6) and sucrose (assigned intensity 3); the standards can be identified by color (yellow for the europate) or hardness (sucrose). An intensity of 1 is assigned to barely detectable emission, and 0 to no detectable light emission under these conditions. This measure of visible intensity is somewhat subjective but reproducible.

The triboluminescence spectrum was obtained using an EG&G PARC OMA III optical multichannel analyzer, spectrometer (Model 1234), and intensified diode array detector (1421HQ,) with Pelletier cooling. A slit width of 100 μm was used (four pixels), giving a resolution of 2.4 nm. Samples were ground with a glass rod in Pyrex test tubes for five blocks of 10 s each.[29]

Photoluminescence spectra were obtained on a Perkin-Elmer MPF-4 , LS-5B, or LS-50 with a resolution of 2−5 nm. All excitations of photoluminescence were carried out at the maxima, 405 ± 14 nm; excitation at shorter wavelength maxima produced weaker but similar emission. No attempt was made to determine whether the emission was phosphorescence or fluorescence.

Triboluminescence, photoluminescence, and crystal structure were all determined using samples from the same batch of crystals in each case.

Results

Crystal Structures. The space group, unit cell, collection and refinement parameters for crystals of compounds **3**, **4**, and **6**−**12** (Figure 1), are reported in Table 1. We have assumed that carboxylic acid **1** has the crystal structure found by Heller and Schmidt.[26] Preliminary data indicated that our samples of **2** have the $P2_1/c$ structure previously reported;[30] thus we used the Cambridge[31] data file MOCANT[30] with the more compact setting of $P2_1/n$ to generate the illustrations in this paper.

Each of the esters **4**, **5**, and **7**−**9** has two groups similar in size and shape at the chiral center to provide a potential source of disorder. We found crystallographic disorder only in the propyl chain of **7**, and could not determine or estimate hydrogen positions. On the basis of a complete data collection and refinement in $P1$ and $P\bar{1}$, crystals of chiral ester **5** were crystallographically indistinguishable from those of **4**, indicating that either its ethyl and methyl groups are disordered or the crystals are twinned. The similarity of crystals in each batch of **5** indicates that we did not just examine crystallographically attractive crystals of a small amount of racemate **4** which might contaminate **5**.

Only chiral **11** was determined to have a noncentrosymmetric space group. Crystals of chiral **5** and **13** are of necessity noncentrosymmetric. We were unable to grow crystals of chiral **13** suitable for crystallographic analysis.

Figures 2−11 show the stacking motifs of the molecules in the solved crystal structures. The acid (**1**) forms flat infinite stacks—the β structure identified by Schmidt and co-workers[26] and illustrated in Figure 12a.

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(29) Sweeting, L. M.; Guido, J. L. *J. Lumin.* **1985**, *33*, 167−173.

(30) Bart, J. C.; Schmidt, G. M. J. *Isr. J. Chem.* **1971**, *9*, 428−435.

(31) Allen, S. H.; Kennard, O. *Chemical Design Automation News* **1993**, *8*, 31.

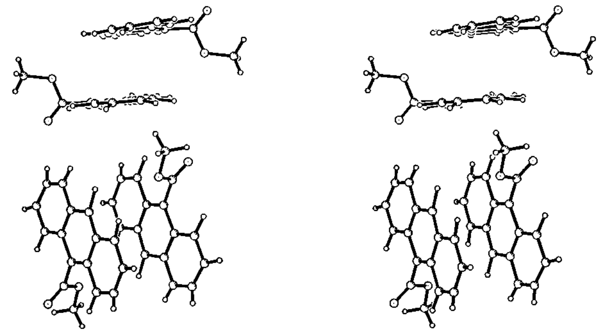

Figure 2. Molecular stacking motif for **2**.

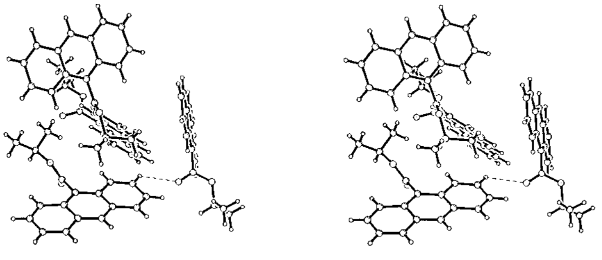

Figure 3. Molecular stacking motif for **3**.

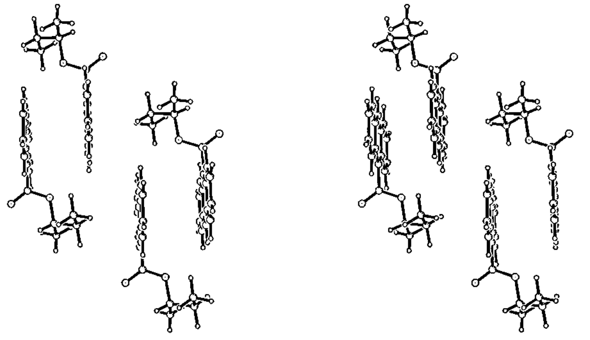

Figure 4. Molecular stacking motif for **4**.

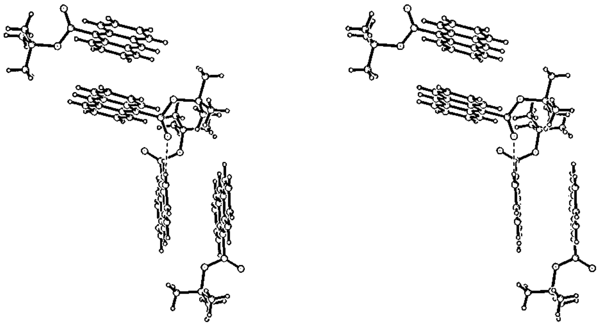

Figure 5. Molecular stacking motif for **6**.

The esters crystallize in three of the other motifs illustrated in Figure 12: esters **3**, **7**, **10**, and **11** form a herringbone of individual molecules (HB, Figure 12c), **2**, **6**, and **8** a herringbone of sandwich pairs (SHB, Figure 12d) and **4**, **9**, and **12** a flattened herringbone of sandwich pairs akin to the β structure (FSHB, Figure 12e). None of the esters crystallized in the γ pattern (Figure 12b) sometimes found for unsubstituted aromatics.[32]

Each SHB or FSHB sandwich of the racemic esters (**4**, **8**, **9**, and **12**) consists of a pair of enantiomers; adjacent sets of enantiomeric pairs face the opposite way, rendering the crystal centrosymmetric. The individual HB stacks of **7** consist of alternating *R* and *S* enantiomers, whereas those of **10** consist of one enantiomer, with the other enantiomer in adjacent stacks.

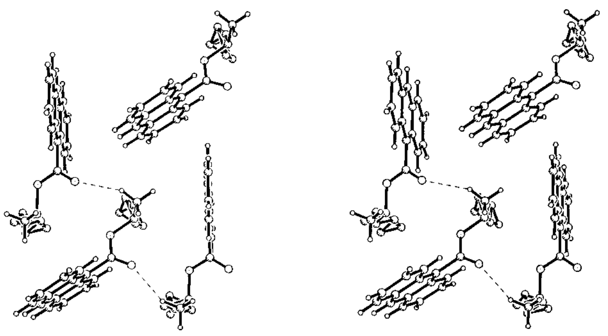

Figure 6. Molecular stacking motif for **7**.

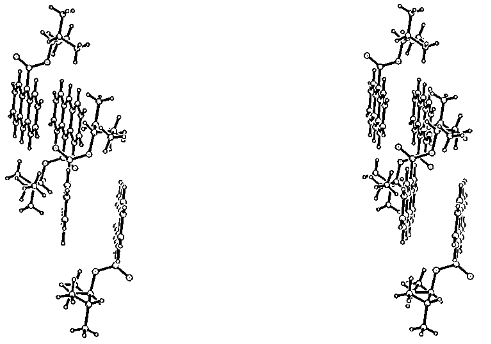

Figure 7. Molecular stacking motif for **8**.

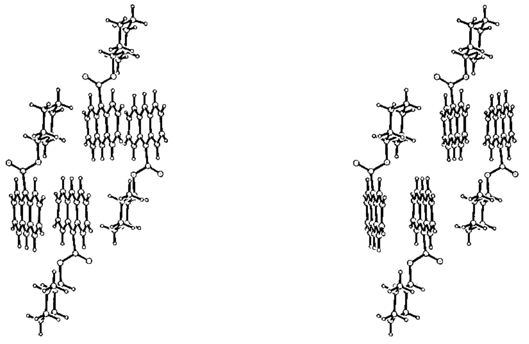

Figure 8. Molecular stacking motif for **9**.

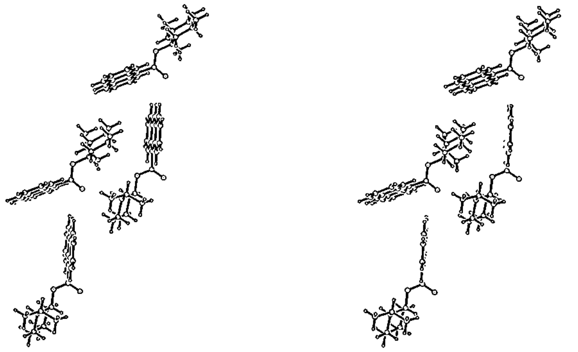

Figure 9. Molecular stacking motif for **10**.

The spacing between sandwich pairs in the SHB and FSHB structures is 3.4−3.6 Å, with all except **9** showing near-ideal ring orientation, in which each anthracene ring is displaced diagonally from its partner in the sandwich so that three carbons of each are centered over the three rings of the other. In **9**, the rings are staggered along the long axis but almost aligned along the short axis, putting pairs of carbons, instead of single carbons, over the center of each ring.

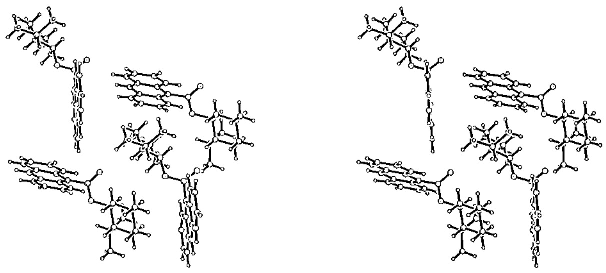

Figure 10. Molecular stacking motif for **11**.

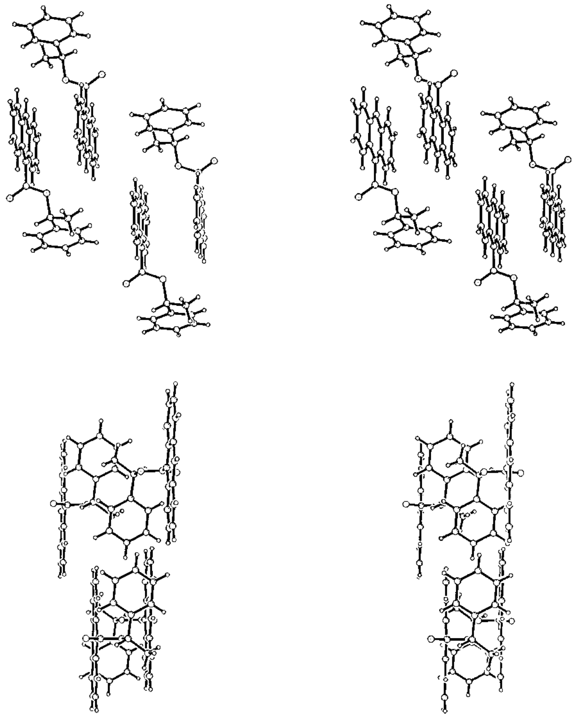

Figure 11. Molecular stacking motif for **12**: (a, top) anthracene $\pi-\pi$ interactions. (b) benzene $\pi-\pi$ interactions.

Photoluminescence. The wavelength maxima and peak widths at half-height of the solid-state photoluminescence emission of **1**−**13** are reported in Table 2, along with some crystallographic and triboluminescence information. We did not determine whether the emissions are fluorescence or phosphorescence and thus will continue to call it photoluminescence.

The photoluminescence emissions of the 9-anthracenecarboxylate family fall into three categories: (1) strong and narrow, with maximum emission at less than 440 nm; (2) strong and broad, with maximum emission at greater than 440 nm; (3) very weak (or no) photoluminescence.

Crystals of **3**, **7**, **10**, and **11** have intense emission at less than 440 nm and emission line widths at half-height of about 45 nm. Only **10** (Figure 13a) shows significant vibrational structure in the emission.

Crystals of esters **8**, **12**, and **13**, and the acid itself (**1**) are intensely photoluminescent, with maxima at wavelengths greater than 440 nm and a width at half-height nearly double that of the esters emitting below 440 nm. Figure 13b shows the excitation and emission spectra of **12**. In dilute solution, the 514 nm emission maximum of **12** shifted to 470 nm in toluene and to 453 nm in methanol; the photoluminescence spectra of the other esters were not measured in solution.

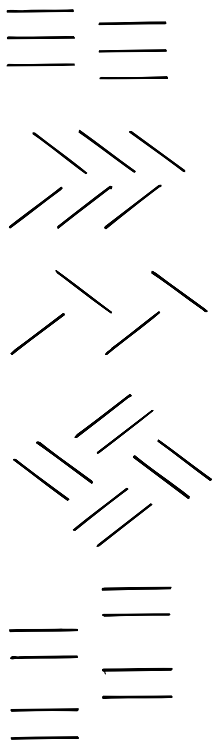

Figure 12. Stacking motifs observed for aromatic compounds. (a) β; (b) γ; (c) herringbone (HB); (d) sandwich herringbone (SHB); (e) flat sandwich herringbone (FSHB).

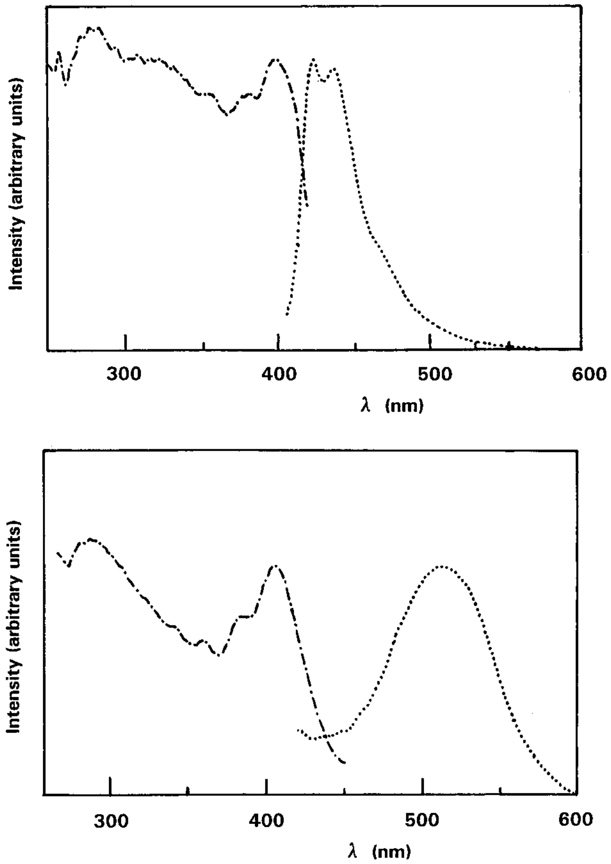

Figure 13. Photoluminescence Spectra, Excitation (— • —) and Emission (•••): (a) **10**, typical herringbone emission; (b) **12**, typical sandwich excimer emission.

Crystals of **4**, **5**, **6**, and **9** have surprisingly weak photoluminescence; moreover, the emissions are broad and at wavelengths longer than 440 nm. Our samples of **2** produced no photoluminescence emission from any of several fresh batches and recrystallizations, although solutions of **2** were strongly photoluminescent; Heller reported excimer emission for **2**.[33] Some old batches (parts of this project were completed over 10 years) of **2** had developed a photoluminescent powder on the surface of one face, but we were unable to obtain its spectrum. We further noted that samples of **2**−**7** became opaque over months or years, often initially in zones; cloudiness in **4** developed a distinct hourglass shape. The photoluminescence spectra of the powdery or opaque samples were indistinguishable from those of the fresh materials.

Triboluminescence. The triboluminescence activity of each ester was tested upon initial crystallization; Table 2 reports these observations as “activity crude”. During the process of purifying the samples for crystallography, we noted that the triboluminescence activity sometimes changed; Table 2 reports the activity after 1−3 further recrystallizations as “activity purified”.

Crude **3**, **4**, **7**, **8**, and **13** had weak triboluminescence emission which disappeared on recrystallization. In an attempt to understand the variations in activity, we contaminated purified, nontriboluminescent **4** and **7** by recrystallizing them from ethanol and cyclohexane in the presence acid **1**, which we believed might be an impurity. The triboluminescence of **4** returned on recrystallization with **1** in both solvents, but that of **7** did not. The photoluminescence of HB **7** was slightly broader after recrystallization with β-sandwich **1**, but that of FSHB **4** was unchanged. We did not attempt contamination experiments on compounds which were never triboluminescent or always triboluminescent. The presence of cloudiness in the crystals was not correlated with triboluminescence activity for the purified compounds.

Crude **10** was strongly triboluminescent and released the odor of racemic menthol when crystallized from cyclohexane but not from ethanol. Both the triboluminescence and the odor of crude **10** decreased with time. The triboluminescence of **10** disappeared after one additional recrystallization from cyclohexane. Racemic menthol was tested and found not to be triboluminescent, although chiral menthol is.[29,34]

The triboluminescence intensity of all samples decreased upon grinding in air. The triboluminescence of crude **11** was tested under 2-propanol, chosen for its ability to wet the surfaces of the crystals without completely dissolving them; the intensity decreased (from 5 to 3) but did not disappear. To evaluate the significance of triboluminescence quenching under liquids, we tested 21 other strongly triboluminescent organic and inorganic crystals under air, hexane, and 2-propanol: 9 retained their triboluminescence, most with reduced intensity, under hexane and 8 under 2-propanol (2 dissolved).[35] The liquid made it more difficult to grind the sample because of lubrication. Because of the intensity reduction, we did not test materials with activities of 3 or less (such as **5**) under liquids.

Figure 13 shows the triboluminescence spectrum of **11** with its solid-state photoluminescence excitation and emission spectra for comparison. The triboluminescence emission maximum is at longer wavelength (455 nm) than the photoluminescence (425 nm). We found no evidence of dinitrogen emission lines in the spectrum of **11**; we estimate that we could have detected dinitrogen emission with a signal height of 0.3% of that of the 455 nm band. We were unable to obtain spectra of tribophotoluminescent samples with intensity equal to or less than that of sucrose (intensity 3, Table 2). Moreover, it is difficult to obtain spectra of soft crystals, such as these esters. Grinding reduces them quickly to a fine powder (and lubricant) whose triboluminescence is much harder to excite; further time averaging of emissions is ineffective at accumulating enough signal for a spectrum.

Discussion

Crystal Packing Motifs. Crystallographically, the compounds in this study may be divided into two sets, in two different ways: centrosymmetric versus noncentrosymmetric space group or herringbone (HB) versus sandwich (SHB, FSHB and β) ring-packing motif. The space group symmetry and its relationship to triboluminescence will be discussed later.

The common ring-packing motifs of crystals of aromatic compounds shown schematically in Figure 12 represent different compromises between stabilization of neighboring aromatic rings by C−H···π nonbonded interactions (edge-to-face) and by π···π nonbonded interactions (face-to-face). Both interactions are most certainly attractive, as they persist both in solution and gas phases, revealing their presence spectroscopically and (stereo)chemically.[36−40]

The β stacking motif (Figure 12a) is most common with aromatic compounds of large area.[32] The hydrogen-bonded pairs of **1** provide sufficient area for the β structure and lateral displacement adequate to prevent solid-state dimerization.[26] None of the esters has the β stacking motif.

Simple herringbone motifs (HB, Figure 12c) with only C−H···π interactions[41] are usually observed for elongated unsubstituted aromatics such as anthracene. HB esters **3**, **7**, **10**, and **11** have modified C−H···π orientations, with the hydrogen atoms of one ring consistently near one edge and close to the carbonyl oxygen of the other (Figures 3, 6, 9, and 10). This arrangement is probably driven both by the need to pack the alkyl groups with maximum density[42] and by attractive interactions, either between the carbonyl oxygen atom and an aromatic C−H or between alkyl C−H groups and the π cloud.[37,43]

Sandwich-herringbone motifs (SHB, Figure 12d), observed with disklike unsubstituted aromatics such as pyrene,[43] have face-to-face paired rings displaced di-

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[32] Desiraju, G. R.; Gavezotti, A. *Acta Crystallogr.* **1989**, *B45*, 473−482.

[33] Heller, E. Ph.D. Thesis, The Weizmann Institute of Science, 1969.

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[42] Brock, C. P.; Dunitz, J. D. *Chem. Mater.* **1994**, *6*, 1118−1127.

[43] Desiraju, G. R. *Acc. Chem. Res* **1991**, *24*, 290−296.

agonally so that carbon atoms are centered over their neighbors' aromatic rings and C−H⋯π interactions between neighboring pairs. SHB esters **2**, **6**, and **8** (Figures 2, 5, and 7) exhibit ideal face-to-face interactions but only **2** has the classic near-perpendicular edge-to-face interactions. Since the herringbone angle in **8** is too small (about 10°) to permit C−H⋯π interactions, its motif is better classified as FSHB.

The flat-sandwich-herringbone motif (FSHB, Figure 12e) does not occur for unsubstituted aromatics, which attain greater density with the β structure. It can be viewed as a special case of either SHB or β. The FSHB motifs of **4**, **8**, and **12** (Figures 4, 7, and 11) have ideal face-to-face interactions but no aromatic edge-to-face interactions of anthracene rings. The phenyl rings of the substituent in FSHB **12**, however, are perpendicular to the anthracene rings, so that the *o*- and *m*-phenyl C−H bonds point at the anthracene ring of the next sandwich and provide an edge-to-face interaction between benzene and anthracene rings (Figure 11a). There is no close face-to-face contact between phenyl rings but the arrangement permits one methyl C−H⋯π interaction with each phenyl (Figure 11b).

The alkyl groups for all of the esters are aligned so that a significant number of their C−H bonds point toward the nearest anthracene ring with the same ideal angle found for aromatic C−H bonds (within 30° of 90°).[44] For example, at least four hydrogen atoms of the cyclohexane ring and its substituents in HB **10** and **11** and seven in FSHB **9** (three on one side and four on the other) are within attractive range of the nearest anthracene ring; for **9**, these additional C−H⋯π interactions may compensate for the less-than-ideal π⋯π interactions. SHB **6** lacks aromatic edge-to-face interactions, but each methyl of each *tert*-butyl group has one near-ideal C−H⋯π interaction with the same neighboring anthracene ring.

Desiraju and Gavezotti recently pointed out that the unit-cell dimensions for unsubstituted polynuclear aromatic compounds reflect the ring-stacking motif.[32] They observed nonoverlapping ranges of shortest unit-cell axes for the four packing motifs (Figure 12a−d) of 27 monoclinic polynuclear aromatic compounds. Because the unit-cell dimensions can be obtained quickly, the ability to predict packing motif from the shortest cell axis might prove to be useful in solving crystal structures. Thus, we tested its predictive power on the esters by comparing the actual packing motifs of **2**−**4** and **6**−**12** to those predicted by the Desiraju and Gavezotti correlation, choosing a shortest axis of 7.5 Å as the crossover dimension from HB to SHB. We found that the length of the shortest unit-cell axis correctly predicts SHB (of which FSHB is a subset) as the dominant ring-stacking motif for these compounds; however, it fails to predict the four HB structures (**3**, **7**, **10**, and **11**). Even this modestly successful prediction of packing motif from shortest cell axis could provide a useful tool in solving crystal structures of other substituted aromatics.

Photoluminescence and Crystal Structure. The solid-state photoluminescence spectra of **3**, **7**, **10**, and **11** are characteristic of the isolated anthracene rings found in their HB structures, with **10** sharp enough to display vibrational fine structure (Figure 13a).

The solid-state photoluminescence spectra of the acid (**1**) and esters **4**, **5**, **6**, **8**, **9**, **12**, and **13** (Figure 13b) have the significant bathochromic shifts and large emission bandwidths characteristic of excimer emission.[26,41,45] The persistence of some shift and broadening of the emission of **12** in solution indicates some aggregation there as well. The crystals exhibiting excimer emission (Table 2) are exactly those with SHB, FSHB, or β packing motifs, with the anthracene rings 3.4−3.6 Å apart. The ring spacing in the sandwiches (or alignment in **9**) shows no correlation with either the wavelength of the emission or its strength. It has been estimated[36] that the best excimer geometry has ideal staggering of the rings (C over ring center) and a 3 Å spacing; since motion is necessary in all crystals to reach this ideal, it is not surprising that the ring spacings do not correlate with spectral parameters.

The photoluminescence emissions of the esters **3**−**13** provide a simpler and more reliable method for identifying the stacking motifs of the crystals than does the examination of the shortest unit-cell axis described above. In fact, SHB or FSHB packing motifs can be distinguished from the HB by eye: the photoluminescence for SHB and FSHB crystals is green to turquoise, compared to blue for the HB crystals. The photoluminescence of the anthracenecarbinols in our previous study fits this pattern as well.[20]

The weak excimer emissions of **4**, **5**, **6**, and **9** provide some insight into the absence of photoluminescence in **2**. Stevens[41] found that HB naphthacene and pentacene also were not photoluminescent at room temperature and pointed out that there are several possible fates for the excimer besides emission, including dimerization and quenching by sandwich pair exciton traps formed by impurities. All of the weak emitters and **2** crystallize with the SHB or FSHB motif, so that dimerization, self- and impurity-quenching are all possible mechanisms for reducing the photoluminescence. Impurities and dimerization will be considered in more detail in the next section but are less likely causes of weak emission than self-quenching.

Triboluminescence, Photoluminescence, and Purity. Triboluminescence activity is relatively common in this series of crystalline compounds but is dependent on sample history (Table 2): 5 of the 10 centrosymmetric materials (**3**, **4**, **7**, **8**, and **10**) are triboluminescent only when impure, as is one of the noncentrosymmetric materials (**13**). **13** is the first reported example of a *noncentrosymmetric* material which is triboluminescent only when impure. It is likely that other examples exist, but investigators may not have continued purification of their noncentrosymmetric materials because triboluminescence activity was expected. Esters **2**, **5**, **6**, **9**, **11**, and **12** exhibit no significant change in triboluminescence or photoluminescence with purification.

The most likely impurity in these compounds is residual acid **1**, the starting material for their synthesis. The restoration of the triboluminescence of purified FSHB **4** upon recrystallization in the presence of **1** in both ethanol and cyclohexane strongly suggests that **1** is the impurity which induces the triboluminescence. The photoluminescence of the simple HB material **7**, however, was broadened slightly after recrystallization

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[44] Gavezzoti, A. *Chem. Phys. Lett.* **1989**, *161*, 67−72.

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with β-sandwich **1**, indicating incorporation or coprecipitation, but the triboluminescence activity was not restored.

Solid-state hydrolysis may also be a source of contamination by **1**. Crystals of **2**−**7** developed a powder on the surface with green photoluminescence or became partially opaque after many months, although no change in triboluminescence activity accompanied formation of this powder. The opacity may be caused by slow solid-state hydrolysis to **1** or oxidation to a quinonoid. The opacity developed in definite zones, particularly a distinct hourglass shape in **4**, indicating a solid-state reaction via specific crystal axes.[46−48]

It is unlikely that the opacity is caused by photochemical dimerization since both SHB/FSHB and HB crystals develop it and the powdery coating is highly photoluminescent. Moreover, we minimized exposure of these compounds to room light to prevent the dimerization.[26,27,49] We succeeded: the solution NMR spectra of these compounds are consistent only with the anthracene structure after many months of standing; however, we would not be able to detect small amounts of dimer. We found no evidence for solvates or polymorphs. We intend to examine the chemical and physical sources of the surface and zone opacity.

The bright triboluminescence of impure **10** can also be traced to contamination by starting material, namely, *racemic* menthol, which is itself neither triboluminescent nor photoluminescent: only samples which released the odor of racemic menthol were triboluminescent. Impure **13** could be contaminated by chiral alcohol or racemic ester **12**, as well as by acid or dimer.

Grinding itself has been shown to generate impurities: it causes chemical reactions responsible for degradation of engineering materials (tribochemistry). Reversible chemical reactions have also been observed upon grinding.[50] We did not detect any increase in triboluminescence with grinding; in fact, the reverse was observed.

Saccharin's triboluminescence is also due to impurities (*p*-toluenesulfonamide and *p*-sulfamoylbenzoic acid),[12] but saccharin's impurities are themselves triboluminescent and the triboluminescence spectrum of saccharin is that of the impurities. The observations on **3**, **4**, **7**, **8**, and **10** clearly demonstrate that photoluminescence, triboluminescence, and chirality are unnecessary for an impurity to induce triboluminescence in the host crystal. Mechanisms by which impurities can affect triboluminescence by altering the crystal structure are discussed below.

Impurities can also increase existing triboluminescence, as they do for ester **11**, by several mechanisms. Wintergreen candy (impure sucrose) triboluminescence is brighter than that of sucrose,[19,51] and that of *N*-isopropylcarbazole is brighter when contaminated with anthracene.[52] In both cases, the triboluminescence spectrum is dominated by the intense visible photoluminescence of the impurity. For wintergreen candy, the predominantly UV dinitrogen emission of sucrose is absorbed by the methyl salicylate to excite its visible photoluminescence, thus shifting the emission into the visible.[19] Filled polymers are more triboluminescent than unfilled because of additional crack tips, and thus charge separation, upon interfacial failure.[53,54] Any mechanisms by which impurities induce triboluminescence can also increase existing triboluminescence.

In principle, impurities could also reduce or quench triboluminescence, for example by acting as exciton traps to quench the photoluminescence. To our knowledge, however, there are no published examples of triboluminescence being quenched by solid-state impurities.

Submerging triboluminescent materials in liquids quenches some triboluminescence. The fact that the triboluminescence of **11** does not disappear when it is submerged in 2-propanol suggests that there is no gas discharge. Of the other crystals we tested, those exhibiting only a discharge triboluminescence lost their activity under both liquids, but some exhibiting both tribophotoluminescence and discharge triboluminescence (e.g., uranyl nitrate hexahydrate) were still active under both liquids, as were most exhibiting only tribophotoluminescence. We conclude that quenching of triboluminescence submerged in a liquid is compelling evidence for a discharge but that the persistence of triboluminescence activity under a liquid is not reliable evidence that a discharge does not occur. The discharge could occur through air trapped or included in the crystal or on its surface. Moreover, cracks propagate at the speed of sound—very high in a solid. Liquid flowing into a crack cannot move as quickly as the propagating crack, so that a pocket of low-pressure air and other vapor persists ahead of the solvent front, in the vicinity of the crack tip where most of the charge is generated;[55] the low-pressure would enhance the intensity of any discharge.[3,56] We thus reject the seductively simple conclusion that a gas discharge does not occur for **11** and other compounds whose triboluminescence is not quenched under a liquid.

Triboluminescence Spectra. The triboluminescence spectra of all the photoluminescent crystals we have studied[17,57] exhibit the photoluminescence spectrum with a small bathochromic shift; **11** fits this pattern (Figure 14). Self-absorption readily accounts for the differences.[20,57] Tribophotoluminescence most likely occurs throughout the crystal as cracks form and must pass through the crystal to reach the detector; photoluminescence, on the other hand, is emitted from the surface, initiated by surface irradiation. The shortest emission wavelengths, which coincide with absorp-

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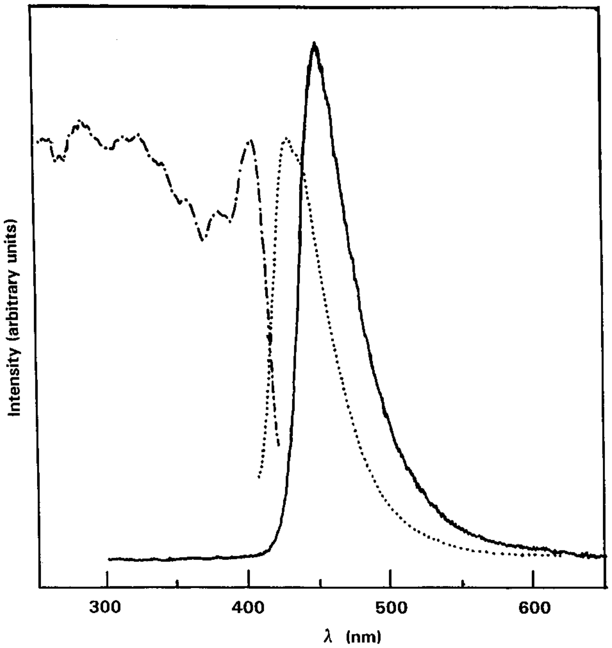

Figure 14. Photoluminescence excitation (— • —) and emission (···) and triboluminescence (—) spectra of **11**.

tion bands, are thus absorbed more during tribophotoluminescence than photoluminescence. Others have proposed that this commonly observed shift is caused by pressure-induced changes in electronic energies;[52,58] however, examination of the triboluminescence spectra of materials whose photoluminescence is pressure-sensitive usually shows that the emission is from species at ambient pressure,[59−61] not from deformed species.

In a few tribophotoluminescent materials, e.g., uranyl nitrate hexahydrate and coumarin, additional emission from an electrical discharge in dinitrogen provides evidence that an electrical discharge occurred. Selective absorption of part of the discharge emission by the crystals further provides evidence that it excited the tribophotoluminescence and is not an independent event.[17,57,62] Its absence, as in **11**, provides no insight into the mechanism of excitation of the photoluminescence: either no discharge occurs or all of the emitted light is absorbed by the crystals.

An electrical discharge could also excite the crystal directly by electron bombardment. Electron bombardment explains the timing of the emission of UV−vis photons, electrons, molecular fragments, and radio signals from the reinforced composites Dickinson et al. have studied under vacuum.[10,63,64] Their studies on pure crystalline materials reveal similar emissions, and a sensitivity of the emissions to crystal axis.[65,66] Their detailed picture of the failure process shows consistent evidence of gas discharge in all cases, but they have not yet examined photoluminescent crystalline materials. It appears that both indirect and direct excitation of the molecules of the crystal may occur, depending on the material, but that the emission spectrum itself may not provide any clear-cut evidence of the source of the excitation.

Triboluminescence and Crystal Structure. Among compounds **1**−**13**, none of the 10 centrosymmetric materials are triboluminescent when purified; two of the three noncentrosymmetric materials, **5** and **11**, are. The existence of a correlation between triboluminescence and crystal symmetry provides compelling evidence for the proposed mechanism of triboluminescence, namely, that charge separation is the primary event and that the piezoelectricity inherent in noncentrosymmetric crystal structures is the most likely source for that charge separation. Two earlier studies also provide strong evidence for a correlation of noncentrosymmetric crystal structure with triboluminescence: the noncentrosymmetric polymorphs of anthranilic acid[12] and nicotinium salicylate[67] are triboluminescent, but the centrosymmetric polymorphs are not. Most attempts to demonstrate this correlation using literature crystal structures, however, have been inconclusive. For example, inorganic sulfates[5] and nitrates[6] generally have triboluminescence in noncentrosymmetric crystals and lack it in centrosymmetric crystals, but 20 of the 46 triboluminescent materials are reported to be centrosymmetric. It is difficult to evaluate whether these 20 triboluminescent materials differed from the materials employed in the crystallography studies. Because we examined the triboluminescence, photoluminescence, and crystal structure using the same batch of crystals, we can be reasonably certain that the crystal whose structure was determined was representative; we found no evidence of polymorphs.

Some pure noncentrosymmetric materials are triboluminescent. Several mechanisms other than piezoelectricity have been proposed to generate the charge separation necessary for triboluminescence in centrosymmetric structures. Dickinson has observed bond ruptures in polymers[68,69] and explosives,[70,71] which release electrons, molecular fragments, and visible and radio emissions.[24,72,73] Ionic compounds may permit charge separation by partial fracture along planes with opposite charges.[2,7,74,75] These mechanisms are unlikely for most organic compounds with their weak intermolecular forces: even sucrose with its strong intermolecular hydrogen bonds does not release molecular fragments.[63] Another possibility that has not previously been considered is that, even in a pure compound,

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deformation may change the local structure from that observed by X-ray diffraction, generating sites of local dissymmetry which can support charge separation. All mechanisms which separate charge for centrosymmetric crystals can do so for noncentrosymmetric crystals as well.

The triboluminescence of centrosymmetric **3**, **4**, **7**, **8**, and **10**, however, is clearly dependent on impurities. None of the impurities we identified are themselves triboluminescent or piezoelectric. In any case, it is unlikely that the crystal symmetry of the impurities would be important, since the low impurity concentration is likely to distribute the impurities as individual molecules and not as incorporated crystallites; molecular chirality, however, should be important. Random impurities may create sites of local dissymmetry or of slightly different ionization potential or electron affinity and thus regions in which charge can accumulate until the field is great enough for discharge; filled polymers provide dramatic examples of this effect.[72,73] It is more likely, however, that specific incorporation of impurities will occur on certain faces during crystal growth, especially since the impurities are probably starting materials remaining in the solution. Selective incorporation onto faces is dramatically illustrated by the formation of colored hourglass shapes when dyes are incorporated into potassium sulfate crystals.[48,76−78] Such selective incorporation reduces the symmetry of the sector, without reducing the bulk symmetry of the crystal;[79] for example, sectors of cinnamide have their symmetry reduced from $P2_1/c$ to $P1$ by incorporation of thienyl acrylamide[80] and to $P2_1$ by cinnamic acid.[79] In these esters, selective incorporation of **1** is possible for all, but especially likely for esters (like **4**) with SHB and FSHB structures. Certain faces of **10** may either incorporate racemic menthol or select one enantiomer (with the other selected at the opposite face), depending on the pattern of enantiomers of racemic **10** which is exposed on the face. Since cracks are intrinsically local, such localized reductions of crystal symmetry could provide a more general mechanism by which impure centrosymmetric crystals could exhibit triboluminescence and a potential method to engineer triboluminescence activity.

Like other workers, we have not attempted to determine whether triboluminescence is caused by deformation or fracture: it is unlikely that these crystals could be fractured without deformation. The importance of deformation for the triboluminescence of crystals of complex molecules has been examined for materials with pressure sensitive photoluminescence spectra: tribophotoluminescence spectra and intensity indicated both high pressure[60] and atmospheric pressure[58,61] at the emitting site. Acenaphthene was reported to emit light on periodic deformation, but the emission was erratic as a function of time rather than periodic, clearly indicating random small fracture events;[81] moreover, its triboluminescence is quenched under 2-propanol and hexane[35] and thus must be dependent on a gas discharge. Only doped salts have been shown to generate triboluminescence by deformation alone: their defects migrate and excite luminescent centers.[2,13,82−85] A similar mechanism in many organics would be consistent with the observed mobility and trapping of excitons in aromatics by impurities or other defects.[86−88] Such a mechanism would not be expected to correlate with crystal symmetry as is usually the case. We are convinced that at least an elastic deformation always occurs and is necessary for piezoelectric polarization but that deformation alone is not the source of the electronic excitation in triboluminescence except in the doped salts. A model requiring fracture is more reasonable.

Superficially it seems that all noncentrosymmetric, and thus piezoelectric, solids ought to be triboluminescent, but there are many examples of noncentrosymmetric materials which, like **13**, lack triboluminescence.[5,6,20,22] For example, only about half of all sugars are triboluminescent (they produce dinitrogen discharge), despite their chirality and piezoelectricity.[9] Apparently charge separation does not guarantee production of either discharge spectrum triboluminescence or tribophotoluminescence. Perhaps some aspect of the crystal packing serves to facilitate charge recombination without excitation of the photoluminescence of air or the crystal.

We found little correlation of packing motif with triboluminescence. Of the intrinsically triboluminescent materials, **5** crystallizes in a sandwich motif (as shown by its excimer photoluminescence) and **11** crystallizes in a simple herringbone (HB). Among those crystals which are triboluminescent when impure, about half are HB and half SHB or FSHB. The sandwich structures are on average more dense than the HB structures. We noted a weak correlation of calculated crystal density (Table 1) with triboluminescence: the most intensely triboluminescent material (**11**) is also the least dense of the noncentrosymmetric crystals; if **13** is like **12**, it would be the most dense and least triboluminescent. A low packing density might permit more incorporation of dinitrogen and a high density might increase conductivity and thus reduce charge separation.

We found no correlation between triboluminescence and any other facets of the crystal structures. We deliberately chose ester alkyl substituents (in **4**, **5**, and **7**−**9**) that might crystallize with some disorder, a property which might provide local dissymmetry sufficient to support charge separation.[15,16] The only disorder observed, for **7,** did not confer any triboluminescence activity.

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Conclusions

Implications for the Mechanism of Tribophotoluminescence. These experiments indicate that a noncentrosymmetric crystal structure *is necessary* for tribophotoluminescence in pure covalent compounds: only noncentrosymmetric pure materials among **1**−**13** are triboluminescent. This correlation was previously illustrated by noncentrosymmetric and centrosymmetric polymorphs of anthranilic acid[12] and nicotinium salicylate.[67] The need for a noncentrosymmetric crystal structure confirms the first step of the mechanism proposed by Longchambon:[18] that the piezoelectricity associated with a noncentrosymmetric structure ensures electrical polarization with pressure and thus the formation of surfaces of opposite charge upon fracture.

In the second step, the voltage is discharged across a gap between oppositely charged surfaces, causing electronic excitation of the molecules of the material, either directly, by electron bombardment, or indirectly, by irradiation with the UV−vis emission of dinitrogen or other vapor molecules excited by electron bombardment. The triboluminescence spectrum of **11**, like that of most photoluminescent materials, contains no detectable emission lines from a dinitrogen discharge nor any indication of an unusual excitation mechanism such as electron bombardment. The persistence of the triboluminescence of **11** under 2-propanol is not inconsistent with a gas discharge, which could occur before the liquid reaches the active crack propagation surface, using dinitrogen trapped in the crystal.

This study demonstrates the importance of impurities to triboluminescence activity, especially for materials which are centrosymmetric, such as **3**, **4**, **7**, **8**, and **10**. We have also discovered that impurities can be necessary to the triboluminescence of noncentrosymmetric materials such as **13**. Crystals of **1**−**13** are no doubt rich in impurities and defects, even after purification. Recent studies of selective incorporation of impurities show that reduction of crystal symmetry can occur for segments of the crystal;[79] in such cases, local cracks may occur in noncentrosymmetric environments in a crystal which is still overall centrosymmetric. Even random impurity incorporation is sufficient to generate local dissymmetry, but this would no doubt be less effective at separating sufficient charge than a symmetry reduction process. This study provides no additional insight into the persistent reports of centrosymmetric triboluminescent materials, but we suggest the purity may be even more important than earlier studies indicated. A study of the nature and distribution of impurities which induce triboluminescence may provide this insight.

It is also clear from this study that a noncentrosymmetric crystal is *not sufficient* to induce triboluminescence. If photoluminescence were absent, self-quenching could be invoked as an explanation. In the case of **13** and other photoluminescent materials, the piezoelectricity may be weak so that little charge is generated, or the crystal may be sufficiently conductive that it cannot support an electric field sufficient to cause gas discharge.[87,88]

By addressing purity and crystal structure in a systematic way, our experiments provide convincing support for the most commonly accepted mechanism of triboluminescence of organic compounds, namely, charge separation from piezoelectricity upon deformation and fracture, followed by excitation of photoluminescence. Experiments to detect the fracture and its products by radio emissions, mass spectrometry, or electron paramagnetic resonance and to determine the role of impurities may resolve some of the remaining questions.

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Supporting Information Available: For **3**−**4** and **6**−**12**, complete lists of atomic coordinates, bond lengths, bond angles, and anisotropic displacement coefficients (52 pages); for **2**−**4** and **6**−**12**, correlation of crystal cell parameters with stacking motif (1 page); and observed and calculated structure factors (46 pages). Ordering information is given on the current masthead page.

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