

4-Vinylbenzoic acid and 9-vinylanthracene

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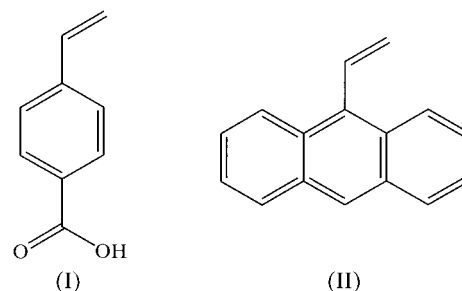
The crystal structures of two styrene analogues, 4-vinylbenzoic acid, C₉H₈O₂, (I), and 9-vinylanthracene, C₁₆H₁₂, (II), were determined by X-ray analyses at 108 and 293 K for (I) and at 123 and 293 K for (II). In (I), a pair of molecules around an inversion center form a dimer connected by two carboxyl groups. The anthracene planes of two molecules in (II) are antiparallel to each other around an inversion center. The vinyl group of (I) is almost coplanar with the phenyl ring, whereas the vinyl group of (II) is nearly perpendicular to the anthracene plane. In (I), the bond length of the vinyl group at 293 K is significantly shorter than that at 108 K [1.288 (2) *versus* 1.3248 (14) Å] suggesting a bias of the thermal motion, whereas the bond lengths are not so different between the two temperatures in (II) [1.3266 (15) *versus* 1.310 (2) Å].

Comment

In the course of the study of solid-state photopolymerization, the title compounds, 4-vinylbenzoic acid, (I), and 9-vinylanthracene, (II), have drawn our attention because they are analogues of styrene, an industrially important monomer compound. Since (I) has a carboxyl group, the molecules are expected to form a dimer structure and it is regarded as a 'straight stick' shape molecule having two vinyl groups at both ends of a 'stick'. The photodimerization of anthracene derivatives is also well known (Sinha *et al.*, 1991). This suggests

that (II) has two possibilities of solid-state photodimerization at the vinyl group and anthracene moiety.

As it is known that the exocyclic vinyl group shows large thermal motion in the crystal form (Tsutsui *et al.*, 1976), the crystal structures of (I) and (II) were determined at low temperature (108 and 123 K, respectively) as well as at room temperature (293 K for both) in order to suppress the thermal motion and to obtain more accurate structures.



The crystal structure of (I) at 108 K is substantially the same as that at 293 K. Two molecules related by an inversion center form a dimer *via* two hydrogen bonds composed of two carboxyl groups as shown in Fig. 1. At both temperatures, the H atom of the carboxyl group is disordered between the O...O bond, and the occupancy factors of the disordered atoms are almost equal. This corresponds to the fact that the C9—O1 and C9—O2 bond lengths are approximately the same due to the disorder. Although the distance between the centers of two adjacent vinyl groups is about 4.1 Å, the two groups do not have a parallel orientation. The vinyl group is almost coplanar with the phenyl ring. The torsion angles between the phenyl ring and vinyl group are almost the same at both temperatures, 9.06 (16)° at 108 K and 9.1 (3)° at 293 K. On the other hand, the bond length of the vinyl group at 293 K is shorter by 0.037 (2) Å than that at 108 K. This may be due to the thermal motion.

In (II), the anthracene moieties of two neighboring molecules related by a center of symmetry are antiparallel as shown in Fig. 2. The vinyl group is not coplanar with the anthracene plane; the torsion angles between the vinyl group and anthracene plane are 56.15 (14)° at 123 K and 58.4 (2)° at 293 K. The distances between the parallel anthracene planes are 3.431 (2) Å at 123 K and 3.506 (2) Å at 293 K. The difference in bond length of the vinyl group at two temperatures, 0.017 (2) Å, is significantly smaller than that observed in (I).

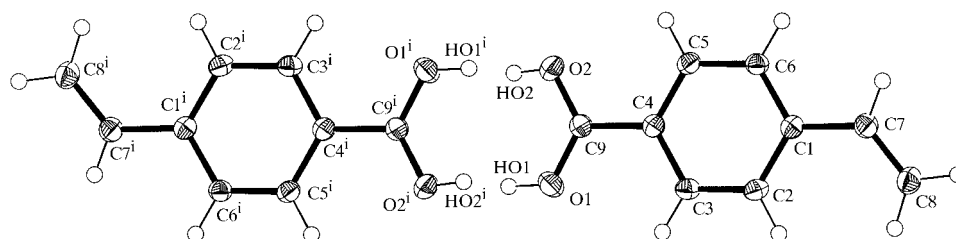
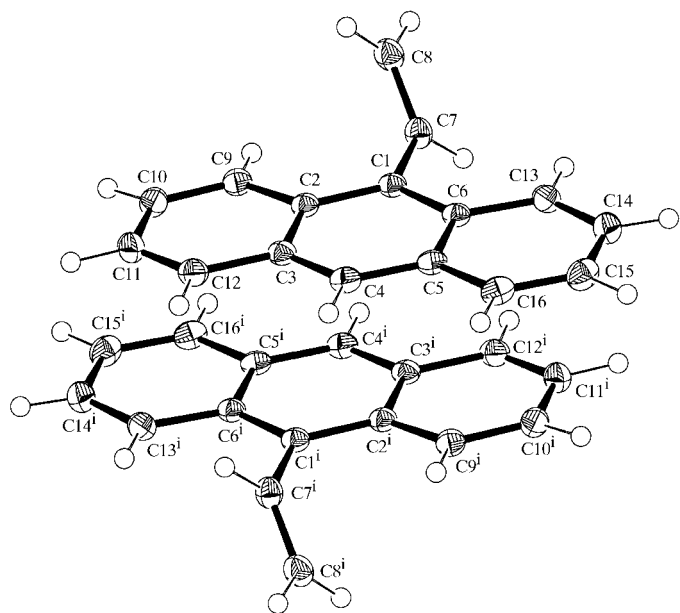


Figure 1

The dimeric structure and center of symmetry in (I) at 108 K with ellipsoids at the 50% probability level. The populations of the HO1 and HO2 atoms are 0.51 (2) and 0.49 (2), respectively. [Symmetry code: (i) 1 - x, 1 - y, 1 - z.]


Figure 2

Two neighboring molecules related by a center of symmetry in (II) at 123 K with ellipsoids at the 50% probability level. The distance between the parallel anthracene planes is 3.431 (2) Å. [Symmetry code: (i) $-x, 2 - y, -z$.]

Experimental

The compounds were purchased from the Aldrich Chemical Company Inc., and crystals were obtained by slow evaporation from *n*-hexane solutions.

Compound (I) at 108 K

Crystal data

$C_9H_8O_2$
 $M_r = 148.15$
 Monoclinic, $P2_1/n$
 $a = 8.3945$ (9) Å
 $b = 6.4096$ (7) Å
 $c = 13.8798$ (14) Å
 $\beta = 103.899$ (4)°
 $V = 724.94$ (13) Å³
 $Z = 4$

$D_x = 1.357$ Mg m⁻³
 Mo $K\alpha$ radiation
 Cell parameters from 9603 reflections
 $\theta = 2.6$ – 27.5 °
 $\mu = 0.096$ mm⁻¹
 $T = 108$ (2) K
 Prism, colorless
 $0.50 \times 0.40 \times 0.30$ mm

Data collection

Rigaku RAXIS-RAPID Imaging Plate diffractometer
 Oscillation photograph scans
 Absorption correction: multi-scan (ABSCOR; Higashi, 1995)
 $T_{min} = 0.952, T_{max} = 0.972$
 6316 measured reflections

1653 independent reflections
 1567 reflections with $I > 2\sigma(I)$
 $R_{int} = 0.034$
 $\theta_{max} = 27.48$ °
 $h = -10 \rightarrow 10$
 $k = -8 \rightarrow 8$
 $l = -18 \rightarrow 17$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.039$
 $wR(F^2) = 0.107$
 $S = 1.054$
 1653 reflections
 129 parameters
 Only coordinates of H atoms refined

$w = 1/[\sigma^2(F_o^2) + (0.0635P)^2 + 0.1621P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{max} < 0.001$
 $\Delta\rho_{max} = 0.38$ e Å⁻³
 $\Delta\rho_{min} = -0.21$ e Å⁻³
 Extinction correction: SHELXL97 (Sheldrick, 1997)
 Extinction coefficient: 0.045 (6)

Table 1

Selected geometric parameters (Å, °) for (I) at 108 K.

O1–C9	1.2703 (12)	C4–C9	1.4813 (13)
O2–C9	1.2667 (12)	C7–C8	1.3248 (14)
C1–C7	1.4734 (14)		
C2–C1–C6	118.39 (9)	C3–C4–C9	120.26 (9)
C2–C1–C7	122.23 (9)	O2–C9–O1	123.38 (9)
C6–C1–C7	119.34 (9)	O2–C9–C4	119.12 (9)
C5–C4–C3	119.57 (9)	O1–C9–C4	117.50 (9)
C5–C4–C9	120.17 (8)		
C8–C7–C1–C2	9.06 (16)	O2–C9–C4–C3	–178.52 (8)
O1–C9–C4–C3	0.99 (14)		

Table 2

Hydrogen-bonding geometry (Å, °) for (I) at 108 K.

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O1–HO1 \cdots O2 ⁱ	0.89 (4)	1.72 (4)	2.6114 (11)	176 (3)
O2–HO2 \cdots O1 ⁱ	0.80 (4)	1.82 (4)	2.6114 (11)	172 (3)

Symmetry code: (i) $1 - x, 1 - y, 1 - z$.

Compound (I) at 293 K

Crystal data

$C_9H_8O_2$
 $M_r = 148.15$
 Monoclinic, $P2_1/n$
 $a = 8.2876$ (16) Å
 $b = 6.5504$ (12) Å
 $c = 14.247$ (2) Å
 $\beta = 102.651$ (8)°
 $V = 754.7$ (2) Å³
 $Z = 4$

$D_x = 1.304$ Mg m⁻³
 Mo $K\alpha$ radiation
 Cell parameters from 8554 reflections
 $\theta = 1.5$ – 27.5 °
 $\mu = 0.092$ mm⁻¹
 $T = 293$ (2) K
 Prism, colorless
 $0.50 \times 0.40 \times 0.30$ mm

Data collection

Rigaku RAXIS-RAPID Imaging Plate diffractometer
 Oscillation photograph scans
 Absorption correction: multi-scan (ABSCOR; Higashi, 1995)
 $T_{min} = 0.982, T_{max} = 0.991$
 5865 measured reflections

1718 independent reflections
 1396 reflections with $I > 2\sigma(I)$
 $R_{int} = 0.054$
 $\theta_{max} = 27.47$ °
 $h = -10 \rightarrow 10$
 $k = -7 \rightarrow 8$
 $l = -18 \rightarrow 18$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.051$
 $wR(F^2) = 0.139$
 $S = 1.071$
 1718 reflections
 129 parameters
 Only coordinates of H atoms refined

$w = 1/[\sigma^2(F_o^2) + (0.0661P)^2 + 0.0872P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{max} < 0.001$
 $\Delta\rho_{max} = 0.18$ e Å⁻³
 $\Delta\rho_{min} = -0.13$ e Å⁻³
 Extinction correction: SHELXL97 (Sheldrick, 1997)
 Extinction coefficient: 0.070 (11)

Table 3

Selected geometric parameters (Å, °) for (I) at 293 K.

O1–C9	1.2611 (19)	C4–C9	1.464 (2)
O2–C9	1.2537 (17)	C7–C8	1.288 (2)
C1–C7	1.462 (2)		
C6–C1–C2	118.13 (14)	C5–C4–C9	121.04 (12)
C6–C1–C7	119.16 (15)	C8–C7–C1	126.40 (18)
C2–C1–C7	122.70 (14)	O2–C9–O1	122.98 (14)
C3–C4–C5	119.24 (14)	O2–C9–C4	118.39 (14)
C3–C4–C9	119.72 (14)	O1–C9–C4	118.63 (13)
C8–C7–C1–C2	9.1 (3)	O2–C9–C4–C3	–178.24 (13)
O1–C9–C4–C3	1.1 (2)		

Table 4
Hydrogen-bonding geometry (Å, °) for (I) at 293 K.

D—H...A	D—H	H...A	D...A	D—H...A
O1—HO1...O2 ⁱ	0.83 (6)	1.79 (6)	2.6043 (17)	166 (5)
O2—HO2...O1 ⁱ	0.87 (7)	1.74 (7)	2.6043 (17)	173 (5)

Symmetry code: (i) 1 - x, 1 - y, 1 - z.

Compound (II) at 123 K

Crystal data

C₁₆H₁₂ *D_x* = 1.269 Mg m⁻³
M_r = 204.26 Mo *K*α radiation
 Monoclinic, *P*2₁/*c* Cell parameters from 12209 reflections
a = 9.3213 (3) Å *b* = 13.6798 (4) Å *c* = 8.8957 (3) Å
β = 109.4670 (10)° *T* = 123 (2) K
V = 1069.48 (6) Å³ Prism, yellow
Z = 4 0.20 × 0.20 × 0.20 mm

Data collection

Rigaku RAXIS-RAPID Imaging 2459 independent reflections
 Plate diffractometer 2231 reflections with *I* > 2σ(*I*)
 Oscillation photograph scans *R*_{int} = 0.033
 Absorption correction: multi-scan *θ*_{max} = 27.48°
 (*ABSCOR*; Higashi, 1995) *h* = -12 → 12
*T*_{min} = 0.975, *T*_{max} = 0.986 *k* = -17 → 17
 10703 measured reflections *l* = -11 → 11

Refinement

Refinement on *F*² *w* = 1/[σ²(*F_o*²) + (0.0626*P*)²
R[*F*² > 2σ(*F*²)] = 0.041 + 0.2677*P*]
wR(*F*²) = 0.115 where *P* = (*F_o*² + 2*F_c*²)/3
S = 1.067 (Δ/σ)_{max} < 0.001
 2459 reflections Δ*ρ*_{max} = 0.31 e Å⁻³
 182 parameters Δ*ρ*_{min} = -0.18 e Å⁻³
 Only coordinates of H atoms Extinction correction: *SHELXL97*
 refined (Sheldrick, 1997)
 Extinction coefficient: 0.062 (6)

Table 5
Selected geometric parameters (Å, °) for (II) at 123 K.

C1—C7	1.4834 (13)	C7—C8	1.3266 (15)
C2—C1—C6	119.79 (8)	C6—C1—C7	118.90 (8)
C2—C1—C7	121.31 (8)	C8—C7—C1	124.56 (9)
C2—C1—C7—C8	56.15 (14)		

Compound (II) at 293 K

Crystal data

C₁₆H₁₂ *D_x* = 1.225 Mg m⁻³
M_r = 204.26 Mo *K*α radiation
 Monoclinic, *P*2₁/*c* Cell parameters from 10475 reflections
a = 9.3873 (5) Å *b* = 13.9756 (10) Å *c* = 8.9889 (7) Å
β = 110.0660 (10)° *T* = 293 (2) K
V = 1107.70 (13) Å³ Prism, yellow
Z = 4 0.40 × 0.30 × 0.30 mm

Data collection

Rigaku RAXIS-RAPID Imaging 2538 independent reflections
 Plate diffractometer 2010 reflections with *I* > 2σ(*I*)
 Oscillation photograph scans *R*_{int} = 0.052
 Absorption correction: multi-scan *θ*_{max} = 27.47°
 (*ABSCOR*; Higashi, 1995) *h* = -12 → 11
*T*_{min} = 0.968, *T*_{max} = 0.976 *k* = -18 → 18
 10621 measured reflections *l* = -11 → 11

Refinement

Refinement on *F*² *w* = 1/[σ²(*F_o*²) + (0.0685*P*)²
R[*F*² > 2σ(*F*²)] = 0.056 + 0.1928*P*]
wR(*F*²) = 0.151 where *P* = (*F_o*² + 2*F_c*²)/3
S = 1.056 (Δ/σ)_{max} < 0.001
 2538 reflections Δ*ρ*_{max} = 0.25 e Å⁻³
 182 parameters Δ*ρ*_{min} = -0.16 e Å⁻³
 Only coordinates of H atoms Extinction correction: *SHELXL97*
 refined (Sheldrick, 1997)
 Extinction coefficient: 0.109 (10)

Table 6
Selected geometric parameters (Å, °) for (II) at 293 K.

C1—C7	1.4857 (19)	C7—C8	1.310 (2)
C6—C1—C2	119.79 (12)	C2—C1—C7	121.39 (13)
C6—C1—C7	118.82 (12)	C8—C7—C1	125.46 (15)
C2—C1—C7—C8	58.4 (2)		

H atoms were located on a difference Fourier map and refined with *U*_{eq} set at 1.2 times that of the connected C or O atom. In (I), the C—H bond lengths range from 0.939 (15) to 0.975 (15) Å at 108 K and from 0.930 (19) to 1.03 (2) Å at 293 K. In (II), the ranges are from 0.972 (14) to 0.995 (13) Å at 123 K and from 0.94 (2) to 1.02 (2) Å at 293 K. The O—H bond lengths in (I) are 0.89 (4) Å for O—HO1 and 0.80 (4) Å for O—HO2 at 108 K, and the distances are 0.83 (6) and 0.87 (7) Å, respectively, at 293 K.

For both compounds, data collection: *PROCESS-AUTO* (Rigaku, 1998); cell refinement: *PROCESS-AUTO*; data reduction: *TEXSAN* (Rigaku, 1999); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1998); software used to prepare material for publication: *SHELXL97*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: OB1035). Services for accessing these data are described at the back of the journal.

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