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Specific Structural Features and Photochemical Properties of Three Benzo-Annulated 2,2-Diphenyl[2H]chromenes

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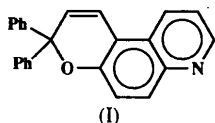
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Abstract

The crystal structures of 3,3-diphenylbenzo[*f*]chromene, C₂₅H₁₈O, 1,3,3-triphenylbenzo[*f*]chromene, C₃₁H₂₂O, and 2,2-diphenylbenzofuro[2,3-*g*]chromene, C₂₇H₁₈O₂, have been determined. Annulated 2,2-diphenylchromenes are of interest because of the influence of steric strain energy in the pyran ring on the photochromic properties of these compounds.

Comment

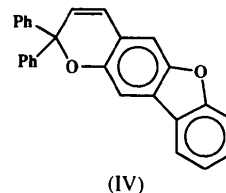
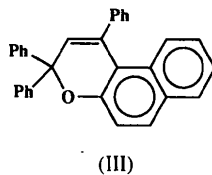
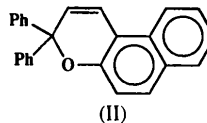
We presented previously (Aldoshin *et al.*, 1995), the results of an X-ray investigation of the 2*H*-chromene derivative (I).



Our interest in this class of compounds is due to the fact that, in contrast to other classes of photochromic compounds like spiropyrans and spirooxazines, 2*H*-chromenes do not contain a spiro-heterocyclic fragment. Nevertheless, some chromenes do possess photo-, thermo- or solvatochromic properties in solution.

The breaking of the C1—O1 bond is responsible for the photochromic properties of chromenes. The X-ray study of the photochromic diphenylchromene (I)

(Aldoshin *et al.*, 1995) has shown that the C1—O1 bond in this compound is elongated due to steric interactions. In order to analyse the influence of substitution on the structure of the pyran ring and to establish a relationship with their photochromic properties, we have determined the X-ray structures of three new compounds, namely, 3,3-diphenylbenzo[*f*]chromene, (II), 1,3,3-triphenylbenzo[*f*]chromene, (III), and 2,2-diphenylbenzofuro[2,3-*g*]chromene, (IV) (Pozzo, 1994).



The main characteristic parameters of compounds (II)–(IV) are reported for comparison in Table 5. In compound (II), the pyran ring is only slightly flattened compared to compound (I), whereas for compounds (III) and (IV) the pyran rings are more non-planar.

The phenyl groups for all three compounds are quite orthogonal. The relative orientations of these phenyl groups with respect to the pyran ring are different; one ring is eclipsed with respect to the O1—C1 bond [(II) O1—C1—C14—C15 14.2 (2); (III) O1—C1—C26—C27 18.2 (3); (IV) O1—C1—C22—C27 14.5 (1)°] and the other is eclipsed with respect to the C1—C2 bonds of the pyran ring [(II) C2—C1—C20—C25 3.2 (2); (III) C2—C1—C20—C25 7.1 (3); (IV) C2—C1—C16—C17 4.5 (1)°]. In compound (I), the O1—C1 and C1—C2 bonds of the pyran ring are in a screw conformation with respect to the phenyl rings [corresponding values are 32.6 (2) and 24.1 (2)°].

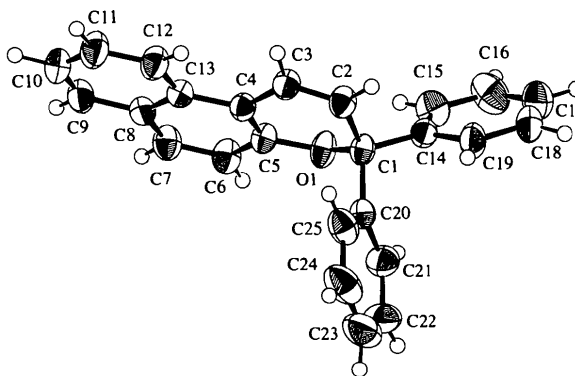


Fig. 1. ORTEP drawing (Johnson, 1976) of compound (II) with displacement ellipsoids at the 50% probability level.

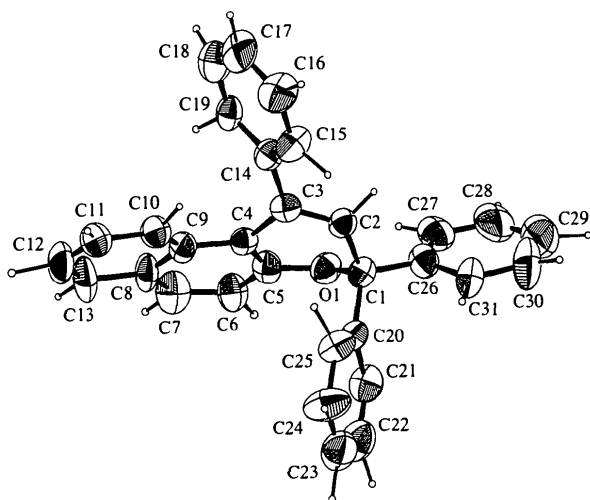


Fig. 2. ORTEP drawing (Johnson, 1976) of compound (III) with displacement ellipsoids at the 50% probability level.

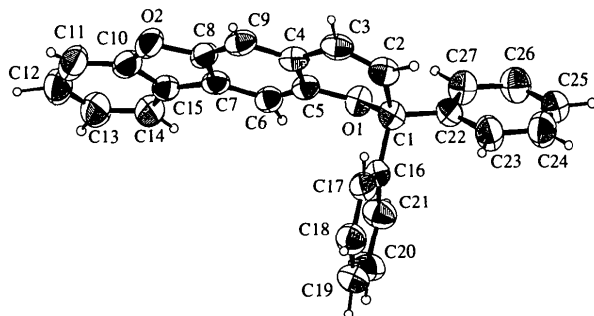
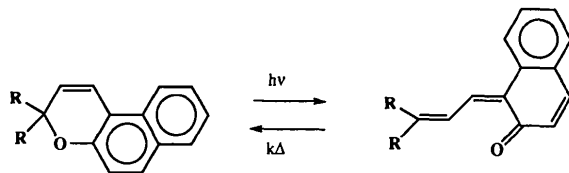


Fig. 3. ORTEP drawing (Johnson, 1976) of compound (IV) with displacement ellipsoids at the 50% probability level.

The photoactivity of photochromic compounds is measured by their 'colourability'. In general, this parameter is determined as the initial absorbance (A_0) measured at the λ_{\max} of the open form (see below) immediately after irradiation under flash-photolysis conditions (Miller, Levoir, Fontaine, Garnier & Dubois, 1975). The results of the photochemical investigation are reported in Table 6 and show that compounds (I), (II) and (IV) are photochromic at room temperature and that their photochromability increases in the order (I) < (II) < (IV).



Using the MMP2 (Allinger & Yuh, 1977) method, the steric strain energies (E_s) of the pyran rings were calculated. This strain energy appeared to correlate with the photochemical activity and increases in the order

(I) < (II) < (IV). The lack of photochromic properties of compound (III) at room temperature, though it displays the highest E_s , can be explained by the steric hindrance of the 4-phenyl group, which can prevent the *cis-trans* isomerization taking place during the photochromic process or can significantly decrease the thermal stability of the coloured form.

Experimental

Compounds (II), (III) and (IV) were synthesised *via* the condensation of 1,1-diphenyl-1-propynol with polyaromatic or heterocyclic phenols (Pozzo, 1994; Cotterill, Livingstone & Walshaw, 1970). Crystals suitable for analysis were obtained by recrystallization from hexane for compound (II) and from heptane for compounds (III) and (IV).

Compound (II)

Crystal data

$C_{25}H_{18}O$
 $M_r = 334.42$
 Monoclinic
 $C2/c$
 $a = 33.979(7) \text{ \AA}$
 $b = 6.3980(10) \text{ \AA}$
 $c = 16.999(3) \text{ \AA}$
 $\beta = 71.69(3)^\circ$
 $V = 3508.4(11) \text{ \AA}^3$
 $Z = 8$
 $D_x = 1.266 \text{ Mg m}^{-3}$
 D_m not measured

Mo $K\alpha$ radiation
 $\lambda = 0.71069 \text{ \AA}$
 Cell parameters from 25 reflections
 $\theta = 10\text{--}20^\circ$
 $\mu = 0.076 \text{ mm}^{-1}$
 $T = 293(2) \text{ K}$
 Needle
 $0.30 \times 0.10 \times 0.05 \text{ mm}$
 Colourless

Data collection

KM-4 diffractometer
 θ scans
 Absorption correction: none
 3793 measured reflections
 3666 independent reflections
 2883 observed reflections
 $[I > 2\sigma(I)]$

$R_{\text{int}} = 0.016$
 $\theta_{\text{max}} = 27.01^\circ$
 $h = -39 \rightarrow 43$
 $k = 0 \rightarrow 8$
 $l = 0 \rightarrow 20$
 3 standard reflections
 frequency: 60 min
 intensity decay: none

Refinement

Refinement on F^2
 $R(F) = 0.050$
 $wR(F^2) = 0.050$
 $S = 1.052$
 3666 reflections
 307 parameters
 Only coordinates of H atoms refined
 Unit weights applied

$(\Delta/\sigma)_{\text{max}} = 0.180$
 $\Delta\rho_{\text{max}} = 0.172 \text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.299 \text{ e \AA}^{-3}$
 Extinction correction: none
 Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Compound (III)

Crystal data

$C_{31}H_{22}O$
 $M_r = 410.51$

Mo $K\alpha$ radiation
 $\lambda = 0.71069 \text{ \AA}$

Monoclinic

$P2_1/c$
 $a = 12.554$ (8) Å
 $b = 10.631$ (7) Å
 $c = 17.393$ (9) Å
 $\beta = 106.12$ (2)°
 $V = 2230$ (2) Å³
 $Z = 4$
 $D_x = 1.223$ Mg m⁻³
 D_m not measured

Cell parameters from 25 reflections
 $\theta = 10\text{--}20^\circ$
 $\mu = 0.072$ mm⁻¹
 $T = 293$ (2) K
 Needle
 $0.30 \times 0.05 \times 0.05$ mm
 Colourless

$S = 0.750$
 3327 reflections
 334 parameters
 Only coordinates of H atoms refined
 Unit weights applied

Extinction correction: none
 Atomic scattering factors from *International Tables for Crystallography* (1992), Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Data collection

KM-4 diffractometer
 θ scans
 Absorption correction: none
 3367 measured reflections
 3241 independent reflections
 1121 observed reflections
 $[I > 2\sigma(I)]$

$R_{\text{int}} = 0.025$
 $\theta_{\text{max}} = 24.02^\circ$
 $h = -14 \rightarrow 13$
 $k = 0 \rightarrow 12$
 $l = 0 \rightarrow 18$
 3 standard reflections
 frequency: 60 min
 intensity decay: none

Refinement

Refinement on F^2
 $R(F) = 0.051$
 $wR(F^2) = 0.051$
 $S = 1.701$
 3241 reflections
 377 parameters
 Only coordinates of H atoms refined
 Unit weights applied

$(\Delta/\sigma)_{\text{max}} = -1.432$
 $\Delta\rho_{\text{max}} = 0.249$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.396$ e Å⁻³
 Extinction correction: none
 Atomic scattering factors from *International Tables for Crystallography* (1992), Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Compound (IV)

Crystal data

C₂₇H₁₈O₂
 $M_r = 374.44$
 Monoclinic
 $P2_1/c$
 $a = 10.531$ (6) Å
 $b = 21.637$ (9) Å
 $c = 8.550$ (7) Å
 $\beta = 99.98$ (2)°
 $V = 1919$ (2) Å³
 $Z = 4$
 $D_x = 1.296$ Mg m⁻³
 D_m not measured

Cu $K\alpha$ radiation
 $\lambda = 1.54178$ Å
 Cell parameters from 25 reflections
 $\theta = 10\text{--}20^\circ$
 $\mu = 0.635$ mm⁻¹
 $T = 293$ (2) K
 Needle
 $0.35 \times 0.10 \times 0.05$ mm
 Colourless

Data collection

KM-4 diffractometer
 θ scans
 Absorption correction: none
 3709 measured reflections
 3327 independent reflections
 2391 observed reflections
 $[I > 2.0\sigma(I)]$

$R_{\text{int}} = 0.0309$
 $\theta_{\text{max}} = 89.68^\circ$
 $h = -10 \rightarrow 10$
 $k = -20 \rightarrow 27$
 $l = 0 \rightarrow 10$
 3 standard reflections
 frequency: 60 min
 intensity decay: none

Refinement

Refinement on F^2
 $R(F) = 0.0432$
 $wR(F^2) = 0.0432$

$(\Delta/\sigma)_{\text{max}} = 0.932$
 $\Delta\rho_{\text{max}} = 0.424$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.373$ e Å⁻³

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²)

		$B_{\text{eq}} = (4/3)\sum_i \sum_j \beta_{ij} a_i \cdot a_j$			
		x	y	z	B_{eq}
(II)	O1	0.14347 (4)	0.1447 (2)	0.93714 (8)	4.79 (4)
	C1	0.11781 (5)	0.3246 (2)	0.93324 (10)	4.03 (4)
	C2	0.14106 (5)	0.4718 (3)	0.86552 (12)	4.62 (4)
	C3	0.18225 (5)	0.4829 (3)	0.84102 (11)	4.62 (4)
	C4	0.20619 (5)	0.3407 (2)	0.87494 (10)	3.97 (4)
	C5	0.18522 (5)	0.1743 (2)	0.92131 (10)	4.08 (4)
	C6	0.20591 (6)	0.0139 (3)	0.94918 (13)	5.02 (4)
	C7	0.24805 (6)	0.0219 (3)	0.93046 (13)	5.11 (5)
	C8	0.27117 (5)	0.1887 (3)	0.88391 (10)	4.42 (4)
	C9	0.31501 (6)	0.1955 (4)	0.86324 (13)	5.33 (5)
	C10	0.33696 (6)	0.3568 (4)	0.81791 (14)	6.01 (5)
	C11	0.31644 (6)	0.5211 (4)	0.7925 (2)	6.32 (6)
	C12	0.27395 (6)	0.5184 (3)	0.81080 (13)	5.42 (5)
	C13	0.25031 (5)	0.3522 (3)	0.85650 (10)	4.17 (4)
	C14	0.08030 (5)	0.2367 (3)	0.91277 (11)	4.32 (4)
	C15	0.07929 (8)	0.0355 (3)	0.88439 (15)	6.01 (5)
	C16	0.04451 (10)	-0.0345 (4)	0.8648 (2)	7.80 (7)
	C17	0.01171 (8)	0.0962 (5)	0.8720 (2)	7.64 (7)
	C18	0.01250 (7)	0.2965 (5)	0.8994 (2)	7.18 (7)
	C19	0.04656 (6)	0.3668 (4)	0.92057 (14)	5.85 (5)
	C20	0.10422 (5)	0.4272 (3)	1.01865 (10)	4.29 (4)
	C21	0.08063 (7)	0.3099 (4)	1.08604 (13)	6.05 (5)
	C22	0.06859 (10)	0.3983 (6)	1.16425 (15)	8.36 (9)
	C23	0.07991 (11)	0.6026 (6)	1.1763 (2)	8.90 (9)
	C24	0.10244 (11)	0.7157 (5)	1.1098 (2)	7.97 (8)
	C25	0.11471 (7)	0.6298 (3)	1.03124 (15)	5.70 (5)
(III)	O1	0.2896 (3)	0.0682 (3)	0.8655 (2)	5.17 (10)
	C1	0.1921 (4)	0.0119 (5)	0.8103 (3)	4.25 (14)
	C2	0.2128 (4)	-0.1273 (5)	0.8073 (4)	4.46 (14)
	C3	0.2683 (4)	-0.1890 (5)	0.8731 (3)	4.35 (14)
	C4	0.3074 (4)	-0.1156 (5)	0.9479 (3)	4.01 (13)
	C5	0.3220 (4)	0.0115 (5)	0.9388 (3)	4.84 (15)
	C6	0.3756 (5)	0.0890 (6)	1.0022 (4)	5.7 (2)
	C7	0.4095 (5)	0.0390 (7)	1.0770 (4)	6.7 (2)
	C8	0.3869 (5)	-0.0863 (7)	1.0920 (3)	5.5 (2)
	C9	0.3343 (4)	-0.1654 (5)	1.0269 (3)	4.71 (14)
	C10	0.3039 (5)	-0.2880 (6)	1.0446 (4)	5.8 (2)
	C11	0.3280 (6)	-0.3304 (8)	1.1219 (5)	7.3 (2)
	C12	0.3839 (6)	-0.2520 (9)	1.1851 (5)	8.0 (2)
	C13	0.4122 (6)	-0.1344 (9)	1.1708 (4)	7.2 (2)
	C14	0.2990 (4)	-0.3224 (5)	0.8666 (3)	4.73 (14)
	C15	0.2253 (5)	-0.4077 (5)	0.8197 (4)	6.1 (2)
	C16	0.2584 (6)	-0.5306 (7)	0.8115 (5)	7.9 (2)
	C17	0.3654 (7)	-0.5694 (6)	0.8496 (5)	8.0 (2)
	C18	0.4382 (7)	-0.4857 (7)	0.8947 (4)	7.1 (2)
	C19	0.4079 (5)	-0.3624 (5)	0.9034 (3)	5.02 (15)
	C20	0.0930 (4)	0.0447 (5)	0.8423 (3)	4.80 (14)
	C21	0.0725 (6)	0.1710 (6)	0.8534 (4)	6.2 (2)
	C22	-0.0151 (6)	0.2027 (8)	0.8839 (4)	7.7 (2)
	C23	-0.0815 (6)	0.1151 (9)	0.9014 (4)	8.6 (2)
	C24	-0.0644 (6)	-0.0096 (7)	0.8896 (5)	8.7 (2)
	C25	0.0235 (5)	-0.0432 (6)	0.8576 (4)	6.5 (2)
	C26	0.1836 (5)	0.0705 (5)	0.7303 (3)	5.4 (2)
	C27	0.2733 (7)	0.1313 (6)	0.7141 (5)	7.2 (2)
	C28	0.2623 (9)	0.1809 (7)	0.6384 (6)	9.5 (3)
	C29	0.1656 (11)	0.1688 (8)	0.5777 (5)	10.9 (3)
	C30	0.0771 (9)	0.1108 (9)	0.5944 (5)	9.9 (3)
	C31	0.0841 (6)	0.0622 (7)	0.6695 (4)	7.5 (2)

(IV)								
O1	0.4289 (2)	0.6238 (1)	0.0420 (2)	4.3 (8)	C1—C20	1.538 (7)	C17—C18	1.358 (9)
O2	0.5923 (2)	0.8543 (1)	-0.0952 (2)	5.3 (10)	C2—C3	1.335 (7)	C18—C19	1.385 (8)
C1	0.2933 (2)	0.6134 (1)	0.0383 (3)	4.1 (10)	C3—C14	1.482 (7)	C20—C25	1.355 (8)
C2	0.2381 (3)	0.6649 (1)	0.1265 (3)	4.9 (12)	C3—C4	1.479 (7)	C20—C21	1.390 (8)
C3	0.2871 (3)	0.7213 (1)	0.1272 (3)	5.4 (12)	C4—C5	1.378 (8)	C21—C22	1.389 (9)
C4	0.3948 (2)	0.7339 (1)	0.0480 (3)	3.3 (11)	C4—C9	1.424 (7)	C22—C23	1.341 (10)
C5	0.4638 (2)	0.6831 (1)	0.0033 (3)	4.0 (10)	C5—C6	1.390 (7)	C23—C24	1.367 (10)
C6	0.5706 (2)	0.6890 (1)	-0.0657 (3)	4.0 (10)	C6—C7	1.361 (9)	C24—C25	1.413 (9)
C7	0.6110 (2)	0.7487 (1)	-0.0952 (3)	4.7 (10)	C7—C8	1.402 (9)	C26—C31	1.397 (8)
C8	0.5409 (3)	0.7988 (1)	-0.0534 (3)	2.9 (11)	C8—C13	1.414 (9)	C26—C27	1.393 (8)
C9	0.4355 (3)	0.7936 (1)	0.0179 (3)	3.6 (12)	C8—C9	1.418 (8)	C27—C28	1.390 (10)
C10	0.6959 (3)	0.8380 (1)	-0.1654 (3)	3.6 (12)	C9—C10	1.415 (8)	C28—C29	1.376 (12)
C11	0.7727 (3)	0.8791 (1)	-0.2298 (4)	8.9 (17)	C10—C11	1.370 (9)	C29—C30	1.371 (13)
C12	0.8705 (3)	0.8544 (2)	-0.2966 (4)	5.1 (17)	C11—C12	1.402 (10)	C30—C31	1.385 (10)
C13	0.8931 (3)	0.7911 (2)	-0.2982 (4)	6.7 (15)	C12—C13	1.341 (10)		
C14	0.8145 (3)	0.7508 (1)	-0.2342 (3)	5.9 (13)	C5—O1—C1	114.3 (4)	C13—C12—C11	120.6 (8)
C15	0.7134 (3)	0.7743 (1)	-0.1674 (3)	4.0 (11)	O1—C1—C26	105.7 (4)	C12—C13—C8	121.1 (8)
C16	0.2283 (2)	0.6078 (1)	-0.1347 (3)	4.3 (10)	O1—C1—C2	107.8 (4)	C15—C14—C19	118.4 (5)
C17	0.1236 (3)	0.6430 (1)	-0.2013 (3)	5.7 (11)	C26—C1—C2	110.2 (5)	C15—C14—C3	121.7 (5)
C18	0.0681 (3)	0.6355 (1)	-0.3607 (3)	5.5 (14)	O1—C1—C20	106.5 (4)	C19—C14—C3	119.7 (5)
C19	0.1174 (3)	0.5934 (2)	-0.4529 (3)	6.7 (16)	C26—C1—C20	112.6 (4)	C14—C15—C16	120.4 (6)
C20	0.2223 (4)	0.5587 (2)	-0.3889 (4)	7.9 (17)	C2—C1—C20	113.6 (4)	C17—C16—C15	120.5 (7)
C21	0.2781 (3)	0.5655 (1)	-0.2292 (3)	6.0 (14)	C3—C2—C1	120.5 (6)	C18—C17—C16	119.3 (7)
C22	0.2847 (2)	0.5519 (1)	0.1263 (3)	4.4 (10)	C2—C3—C14	119.3 (5)	C17—C18—C19	121.5 (7)
C23	0.1647 (3)	0.5247 (1)	0.1172 (4)	6.2 (15)	C2—C3—C4	117.5 (5)	C18—C19—C14	120.0 (6)
C24	0.1519 (3)	0.4705 (2)	0.2008 (4)	6.2 (17)	C14—C3—C4	122.8 (5)	C25—C20—C21	119.0 (6)
C25	0.2586 (3)	0.4430 (1)	0.2893 (3)	7.3 (14)	C5—C4—C9	118.1 (5)	C25—C20—C1	123.0 (5)
C26	0.3762 (3)	0.4704 (1)	0.2999 (4)	6.3 (15)	C5—C4—C3	116.1 (5)	C21—C20—C1	118.0 (5)
C27	0.3905 (3)	0.5250 (1)	0.2193 (3)	6.0 (12)	C9—C4—C3	125.8 (5)	C22—C21—C20	118.9 (7)
					C4—C5—O1	121.6 (5)	C23—C22—C21	121.8 (7)
					C4—C5—C6	122.8 (6)	C22—C23—C24	120.4 (7)
					O1—C5—C6	115.5 (5)	C23—C24—C25	118.5 (7)
					C7—C6—C5	118.7 (6)	C20—C25—C24	121.2 (6)
					C6—C7—C8	121.6 (6)	C31—C26—C27	118.7 (6)
					C7—C8—C13	121.5 (7)	C31—C26—C1	119.6 (6)
					C7—C8—C9	119.2 (6)	C27—C26—C1	121.7 (6)
					C13—C8—C9	119.3 (7)	C28—C27—C26	119.6 (8)
					C4—C9—C10	123.2 (5)	C29—C28—C27	121.7 (9)
					C4—C9—C8	118.9 (5)	C30—C29—C28	118.3 (8)
					C10—C9—C8	117.7 (6)	C29—C30—C31	121.7 (9)
					C11—C10—C9	121.2 (7)	C30—C31—C26	120.0 (8)
					C10—C11—C12	119.9 (8)		

Table 2. Selected geometric parameters (Å, °) for (II)

O1—C5	1.372 (2)	C10—C11	1.402 (3)
O1—C1	1.458 (2)	C11—C12	1.378 (3)
C1—C2	1.505 (2)	C12—C13	1.410 (2)
C1—C20	1.527 (2)	C14—C15	1.379 (3)
C1—C14	1.530 (2)	C14—C19	1.389 (3)
C2—C3	1.331 (2)	C15—C16	1.398 (3)
C3—C4	1.455 (2)	C16—C17	1.368 (4)
C4—C5	1.382 (2)	C17—C18	1.367 (4)
C4—C13	1.434 (2)	C18—C19	1.390 (3)
C5—C6	1.407 (2)	C20—C25	1.379 (3)
C6—C7	1.366 (3)	C20—C21	1.393 (3)
C7—C8	1.412 (3)	C21—C22	1.383 (4)
C8—C9	1.419 (2)	C22—C23	1.395 (6)
C8—C13	1.422 (2)	C23—C24	1.357 (5)
C9—C10	1.362 (3)	C24—C25	1.382 (4)
C5—O1—C1	118.6 (1)	C12—C11—C10	120.5 (2)
O1—C1—C2	110.6 (1)	C11—C12—C13	120.6 (2)
O1—C1—C20	107.6 (1)	C12—C13—C8	118.6 (2)
C2—C1—C20	112.8 (1)	C12—C13—C4	122.3 (2)
O1—C1—C14	105.9 (1)	C8—C13—C4	119.0 (2)
C2—C1—C14	109.3 (2)	C15—C14—C19	118.8 (2)
C20—C1—C14	110.5 (1)	C15—C14—C1	122.5 (2)
C3—C2—C1	121.4 (2)	C19—C14—C1	118.7 (2)
C2—C3—C4	120.4 (2)	C14—C15—C16	119.9 (2)
C5—C4—C13	118.7 (2)	C17—C16—C15	120.6 (2)
C5—C4—C3	117.1 (2)	C16—C17—C18	120.1 (2)
C13—C4—C3	123.9 (2)	C17—C18—C19	119.9 (2)
O1—C5—C4	122.3 (2)	C18—C19—C14	120.7 (2)
O1—C5—C6	115.4 (1)	C25—C20—C21	119.2 (2)
C4—C5—C6	122.1 (2)	C25—C20—C1	122.4 (2)
C7—C6—C5	119.5 (2)	C21—C20—C1	118.3 (2)
C6—C7—C8	121.1 (2)	C22—C21—C20	119.4 (3)
C7—C8—C9	121.2 (2)	C23—C22—C21	120.8 (3)
C7—C8—C13	119.5 (2)	C24—C23—C22	119.1 (2)
C9—C8—C13	119.3 (2)	C23—C24—C25	120.8 (3)
C10—C9—C8	120.6 (2)	C20—C25—C24	120.6 (3)
C9—C10—C11	120.4 (2)		

Table 3. Selected geometric parameters (Å, °) for (III)

O1—C5	1.367 (6)	C14—C15	1.388 (7)
O1—C1	1.458 (6)	C14—C19	1.404 (7)
C1—C26	1.500 (8)	C15—C16	1.390 (9)
C1—C2	1.505 (7)	C16—C17	1.386 (10)

Table 4. Selected geometric parameters (Å, °) for (IV)

O1—C1	1.441 (3)	C20—C21	1.398 (4)
O2—C8	1.389 (3)	C22—C27	1.380 (4)
C1—C2	1.517 (3)	C26—C27	1.389 (3)
C1—C22	1.539 (3)	O1—C5	1.390 (3)
C4—C9	1.399 (3)	O2—C10	1.379 (4)
C6—C7	1.397 (3)	C1—C16	1.523 (4)
C7—C8	1.393 (3)	C2—C3	1.325 (3)
C8—C9	1.360 (4)	C3—C4	1.444 (4)
C10—C11	1.379 (4)	C4—C5	1.407 (3)
C11—C12	1.370 (5)	C5—C6	1.364 (3)
C12—C13	1.391 (6)	C7—C15	1.443 (4)
C13—C14	1.379 (5)	C10—C15	1.391 (3)
C14—C15	1.389 (4)	C16—C21	1.383 (3)
C16—C17	1.379 (4)	C22—C23	1.384 (4)
C17—C18	1.396 (4)	C23—C24	1.392 (5)
C18—C19	1.365 (4)	C24—C25	1.376 (4)
C19—C20	1.369 (5)	C25—C26	1.362 (4)
C1 O1 C5	116.2 (2)	C8—O2—C10	105.3 (2)
O1—C1—C2	109.8 (2)	O1—C1—C16	108.1 (2)
O1—C1—C22	105.5 (2)	C2—C1—C16	113.3 (2)
C2—C1—C22	109.4 (2)	C16—C1—C22	110.6 (2)
C1—C2—C3	119.8 (2)	C2—C3—C4	120.6 (2)
C3—C4—C5	117.7 (2)	C3—C4—C9	123.4 (2)
C5—C4—C9	118.8 (2)	O1—C5—C4	119.1 (2)
O1—C5—C6	117.5 (2)	C4—C5—C6	123.2 (2)
C5—C6—C7	117.7 (2)	C6—C7—C8	118.8 (2)
C6—C7—C15	134.9 (2)	C8—C7—C15	106.2 (2)
O2—C8—C7	111.1 (2)	O2—C8—C9	124.8 (2)
C7—C8—C9	124.1 (2)	C4—C9—C8	117.3 (2)
O2—C10—C11	124.9 (3)	O2—C10—C15	112.0 (2)
C11—C10—C15	123.1 (3)	C10—C11—C12	116.8 (3)
C11—C12—C13	122.1 (3)	C12—C13—C14	120.2 (3)

C13—C14—C15	119.2 (3)	C7—C15—C10	105.3 (2)
C7—C15—C14	135.9 (3)	C10—C15—C14	118.7 (2)
C1—C16—C17	123.3 (2)	C1—C16—C21	117.9 (2)
C17—C16—C21	118.8 (2)	C16—C17—C18	120.5 (2)
C17—C18—C19	120.3 (3)	C18—C19—C20	119.8 (3)
C19—C20—C21	120.4 (3)	C16—C21—C20	120.2 (3)
C1—C22—C23	118.1 (2)	C1—C22—C27	122.4 (2)
C23—C22—C27	119.4 (2)	C22—C23—C24	119.9 (3)
C23—C24—C25	120.3 (3)	C24—C25—C26	119.7 (3)
C25—C26—C27	120.9 (3)	C22—C27—C26	119.9 (3)

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Anthracene-1,8-dicarboxylic Acid

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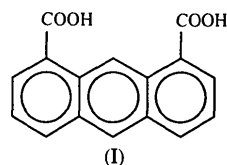
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Abstract

Anthracene-1,8-dicarboxylic acid, C₁₆H₁₀O₄, crystallized in the noncentrosymmetric space group *P*2₁2₁2₁. The carboxyl H and O atoms are ordered. The carboxyl groups make angles of 13.9 (2) and 21.6 (2)° with the best-fit core plane and the average distance of the core atoms from this plane is 0.018 (12) Å. The anthracene core displays near twofold symmetry. Each molecule is involved in cyclic-dimer hydrogen bonding with two other molecules so as to form zigzag chains of hydrogen-bonded molecules which are not cross-linked with one another. These discrete chains are separated from each other by C···C, C···H and H···H closest approaches.

Comment

The present study of anthracene-1,8-dicarboxylic acid, (I), was undertaken as part of a continuing investigation of hydrogen bonding in aromatic carboxylic acids. The assignment of this structure in the noncentrosymmetric space group *P*2₁2₁2₁ makes it of interest for its potential utility in nonlinear optics (Prasad & Williams, 1991).



The carboxyl H atoms in (I) (Fig. 1) are ordered. In the C15 carboxyl group, the C—O distances are 1.318 (8) and 1.202 (7) Å, while in the C16 carboxyl group they are 1.324 (6) and 1.209 (6) Å, consistent with single and double bonds, respectively. Moreover, the carboxyl O atoms are ordered; the principal displacement tensor axes of the O atoms are nearly perpendicular to the carboxyl group planes, as observed previously for ordered carboxyl O atoms in 1- and 2-naphthoic acid (Fitzgerald & Gerkin, 1993).

For the two carboxyl groups, the differences of the pairs of C_{ring}—C—O angle values ($\Delta\theta$) and carboxyl C—O distances (Δr) within each group are such that the two pairs of $|\Delta\theta|$ and $100|\Delta r|$ values bracket closely

Table 5. A comparison of the main characteristic geometrical parameters (Å, °) of chromenes (I)–(IV)

	(I) ^a	(II)	(III)	(IV)
O1—C1	1.458 (4)	1.458 (2)	1.458 (6)	1.441 (3)
O1—C5	1.364 (4)	1.372 (2)	1.367 (6)	1.390 (3)
Bending angle along O1···C2	23.2 (2)	22.8 (2)	31.0 (3)	27.0 (3)
Bending angle along O1···C3	12.2 (2)	9.6 (2)	19.7 (3)	15.8 (3)

Reference: (a) Aldoshin *et al.* (1995).

Table 6. Photochemical data and calculated steric strain energy (E_s) values of the pyran rings in compounds (I)–(IV)

	λ_{\max} (nm)	A_0	E_s (kcal mol ⁻¹) [†]
(I)‡	436	0.77	9.92
(II)	432	0.84	10.19
(III)	Non-photochromic		15.2
(IV)	427/452	1.43/1.39	13.14

† 1 cal = 4.184 J. ‡ Aldoshin *et al.* (1995).

For all compounds, program(s) used to solve structures: *SHELXS86* (Sheldrick, 1985). Program(s) used to refine structures: *SHELXL93* (Sheldrick, 1993) for (II) and (III); *SHELX76* (Sheldrick, 1976) for (IV). For all compounds, molecular graphics: *ORTEPII* (Johnson, 1976).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited for all three title compounds with the IUCr (Reference: PA1201). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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