CRYSTAL AND MOLECULAR STRUCTURE OF *cis*-2,2′,3′,2″-TETRAACETOXY-1,1′:4′,1″-TERNAPHTHYL

Jaroslav PODLAHA[a1], Ivana CISAROVA[a2], Martin BELOHRADSKY[b1] and Jiri ZAVADA[b2]

[a] *Department of Inorganic Chemistry, Charles University, 128 40 Prague 2, Czech Republic;*
  e-mail: [1] *podlaha@prfdec.natur.cuni.cz,* [2] *cisarova@prfdec.natur.cuni.cz*

[b] *Institute of Organic Chemistry and Biochemistry, Academy of Sciences of Czech Republic,*
  166 10 Prague 6, Czech Republic; e-mail: [1] *martinb@uochb.cas.cz,*
  [2] *zavada@uochb.cas.cz*

The configuration and conformation of the title compound as a representative of conformationally locked ternaphthyls was determined by single-crystal X-ray diffraction. The arrangement of the mean planes of naphthyl and acetoxy groups results from intramolecular van der Waals forces.
Key words: Ternaphthyls, conformationally locked; Single crystal X-ray diffraction.

The reaction of 1,4-dibromo-2,3-dihydroxynaphthalene with the 2-naphthoxide anion resulted in the isolation[1] of two conformationally locked isomers of the condensation product, 2,2′,3′,2″-tetrahydroxy-1,1′:4′,1″-ternaphthyl. The isomers could be identified by single-crystal X-ray analysis[1] but the structure determination was rather imprecise since the solvated crystals available exhibited poor diffraction power and/or solvent disorder. Although this seems to be the general problem with derivatives of this family, it was eventually found that the tetraacetate of the *cis*-isomer[1] forms single crystals which enable to determine, with a reasonable degree of precision, the molecular conformation of the novel tetrasubstituted ternaphthyl moiety. The determination of crystal structure of the tetraacetate is the subject of this communication.

EXPERIMENTAL

Crystal and measurement data: $C_{38}H_{28}O_8$, m.w. 612.60, orthorhombic, space group $Pna2_1$ (No. 33), $a = 8.499(2)$, $b = 16.347(3)$, $c = 23.052(7)$ Å, $V = 3\ 202.7(14)$ Å^3, $Z = 4$, $D_{calc} = 1.270$ g cm^{-3}, $F(000) = 1\ 280$. A colourless plate-like crystal of the dimensions $0.45 \times 0.32 \times 0.12$ mm (grown from CH_2Cl_2–heptane by slow evaporation) was measured at 293(2) K on a CAD4 diffractometer with graphite-monochromated MoKα radiation ($\lambda = 0.71073$ Å). Absorption was neglected ($\mu = 0.09$ mm^{-1}). The cell parameters were determined from 25 reflections in the 8–13° θ-range. The intensities of reflections were measured by the θ–2θ scan between $h \langle 0,9 \rangle$, $k \langle 0,17 \rangle$, $l \langle 0,25 \rangle$, $\theta_{max} = 25°$. Three standard reflections monitored every 1 h showed intensity variation between –4 and

Atomic coordinates (. 10^4) and equivalent isotropic displacement parameters (Å^2 . 10^3) with estimated standard deviations in parentheses. U_{eq} is defined as one third of the trace of the orthogonalized $\boldsymbol{U}_{ij}$ tensor

Atom	x	y	z	U_{eq}
C1	1220(10)	5329(5)	5000	47(2)
C2	153(9)	4806(5)	5256(4)	45(2)
C3	–419(10)	4941(7)	5808(4)	59(3)
C4	69(12)	5590(6)	6114(4)	65(3)
C5	1787(12)	6795(6)	6217(4)	67(3)
C6	2861(13)	7323(7)	5994(5)	76(3)
C7	3417(13)	7193(7)	5423(5)	76(3)
C8	2885(11)	6566(6)	5099(4)	61(2)
C9	1784(10)	6012(5)	5323(3)	51(2)
C10	1189(11)	6134(6)	5891(4)	55(2)
C11	1793(9)	5185(5)	4397(3)	42(2)
C12	857(10)	5373(5)	3930(4)	49(2)
C13	1416(9)	5305(5)	3364(3)	44(2)
C14	2883(9)	5039(5)	3245(3)	43(2)
C15	5464(9)	4550(5)	3623(4)	45(2)
C16	6389(9)	4357(5)	4085(4)	52(2)
C17	5818(10)	4420(6)	4645(4)	54(2)
C18	4334(9)	4684(5)	4748(4)	49(2)
C19	3341(9)	4891(5)	4289(3)	45(2)
C20	3880(8)	4816(5)	3715(3)	39(2)
C21	3483(10)	4977(5)	2630(3)	47(2)
C22	3616(10)	4243(6)	2374(4)	54(2)
C23	4158(12)	4137(7)	1799(4)	72(3)
C24	4493(12)	4819(8)	1492(4)	73(3)
C25	4833(19)	6331(10)	1430(6)	120(5)
C26	4792(28)	7060(10)	1678(8)	158(8)
C27	4304(22)	7143(9)	2245(8)	138(6)
C28	3847(14)	6471(6)	2561(5)	85(3)
C29	3873(10)	5682(6)	2311(4)	60(2)
C30	4381(12)	5603(8)	1730(4)	72(3)
C31	325(14)	3436(7)	4997(6)	80(3)
C32	–1026(12)	6411(7)	3994(5)	76(3)
C33	–799(11)	5014(7)	2770(4)	57(2)
C34	2070(11)	3086(6)	2611(4)	61(2)
C35	–373(16)	2792(7)	4642(7)	118(5)
C36	–2765(12)	6560(8)	4071(8)	116(5)
C37	–1859(12)	5372(8)	2338(5)	89(4)
C38	1976(14)	2400(6)	3007(5)	89(3)

TABLE I
(*Continued*)

Atom	x	y	z	U_{eq}
O1	−380(6)	4138(4)	4936(3)	58(2)
O2	−693(6)	5618(3)	4017(2)	48(1)
O3	391(6)	5536(4)	2913(2)	54(2)
O4	3371(7)	3546(4)	2706(3)	61(2)
O5	1502(12)	3349(5)	5291(5)	126(3)
O6	−49(9)	6912(5)	3904(6)	125(4)
O7	−908(8)	4367(4)	3007(3)	71(2)
O8	1154(9)	3241(5)	2241(3)	84(2)

+3%. Of 2 293 measured reflections, 2 292 were unique (R_{int} = 0.045) and 1 389 were regarded as "observed" according to the $I \geq 2\sigma(I)$ criterion.

   Data treatment[2,3]: the structure was solved by direct methods (SHELXS86) and refined by SHELXL93 using a full-matrix least-squares procedure based on F^2. Hydrogen atoms were placed in theoretical positions and given the temperature factors of their bonding carbons multiplied by 1.5. The refinement was anisotropic for carbons and oxygens and isotropic for hydrogens. The function minimized was $\Sigma w(F_o^2 - F_c^2)^2$, where $w = 1/[\sigma^2(F_o^2) + (0.1120P)^2 + 1.30P]$, $P = (F_o^2 + 2F_c^2)/3$. Convergence for observed reflections and 415 parameters was achieved at R = 0.0571, R_w = 0.1417, GOF = 1.031, $(\Delta/\sigma)_{max}$ = ±0.001 for non-H atoms. The final difference electron density map was featureless with extremum values of ±0.21 e Å^{-3}. The tables of the observed and calculated structure factors, hydrogen atom coordinates and of the anisotropic displacement parameters, as well as the standard CIF file produced by SHELXL93, can be obtained from the authors upon request.

RESULTS AND DISCUSSION

The final atomic coordinates are given in Table I and the bond distances and angles in Table II. A perspective view of the molecule with atom numbering is depicted in Fig. 1; the crystal packing is obvious from Fig. 2. Somewhat unexpectedly, no analogous ternaphthyl structures could be found in Cambridge Structural Database[2]. In the present structure, the bond distances and angles are unexceptional and require no comment. Of interest, however, is the mutual orientation of the naphthyl and acetoxy groups. The naphthyl groups are planar within ±0.05 Å and the dihedral angles between their least-squares mean planes are 74.7(7), 63.3(6) and 28.3(6)° for the planes involving C1 vs C11, C11 vs C21 and C1 vs C21, respectively. The planes of the terminal naphthyls thus exhibit remarkable mutual twisting, probably as a result of the crowding imposed by the acetoxy groups. As expected, the acetoxy groups are also planar (within ±0.02 Å) and oriented so as to minimize the crowding: they are nearly perpendicular to the adjacent naphthyls, the maximal deviation of the corresponding dihedral angle from

TABLE II
Bond lengths (Å) and angles (°) with estimated standard deviations in parentheses

Atoms	Bond lengths	Atoms	Bond angles
C1–C2	1.379(11)	C2–C1–C9	118.9(5)
C1–C9	1.424(11)	C2–C1–C11	121.0(7)
C1–C11	1.492(8)	C9–C1–C11	120.1(7)
C2–C3	1.382(13)	C1–C2–C3	121.7(8)
C2–O1	1.392(10)	C1–C2–O1	118.3(7)
C3–C4	1.338(14)	C3–C2–O1	119.9(8)
C4–C10	1.400(13)	C4–C3–C2	120.2(9)
C5–C6	1.357(14)	C3–C4–C10	121.4(9)
C5–C10	1.411(13)	C6–C5–C10	121.9(9)
C6–C7	1.41(2)	C5–C6–C7	118.8(9)
C7–C8	1.346(13)	C8–C7–C6	121.3(10)
C8–C9	1.402(12)	C7–C8–C9	120.7(9)
C9–C10	1.418(12)	C8–C9–C10	119.2(9)
C11–C12	1.373(11)	C8–C9–C1	122.6(7)
C11–C19	1.423(8)	C10–C9–C1	118.2(8)
C12–02	1.391(10)	C4–C10–C5	122.5(8)
C12–C13	1.394(11)	C4–C10–C9	119.4(9)
C13–C14	1.348(8)	C5–C10–C9	118.1(9)
C13–O3	1.408(9)	C12–C11–C19	118.3(6)
C14–C20	1.423(10)	C12–C11–C1	120.4(7)
C14–C21	1.510(11)	C19–C11–C1	121.3(6)
C15–C16	1.361(11)	C11–C12–O2	120.0(7)
C15–C20	1.431(10)	C11–C12–C13	121.2(7)
C16–C17	1.383(12)	O2–C12–C13	118.7(7)
C17–C18	1.355(12)	C14–C13–C12	122.1(6)
C18–C19	1.396(11)	C14–C13–O3	120.6(6)
C19–C20	1.405(10)	C12–C13–O3	117.3(6)
C21–C22	1.343(12)	C13–C14–C20	118.6(6)
C21–C29	1.406(12)	C13–C14–C21	121.7(6)
C22–O4	1.388(10)	C20–C14–C21	119.8(6)
C22–C23	1.412(13)	C16–C15–C20	119.8(8)
C23–C24	1.350(14)	C15–C16–C17	120.7(8)
C24–C30	1.40(2)	C18–C17–C16	121.0(8)
C25–C26	1.32(2)	C17–C18–C19	120.4(8)
C25–C30	1.43(2)	C18–C19–C20	119.8(7)
C26–C27	1.38(2)	C18–C19–C11	120.5(6)
C27–C28	1.37(2)	C20–C19–C11	119.7(6)
C28–C29	1.414(14)	C19–C20–C14	120.0(6)

TABLE II
(*Continued*)

| Atoms	Bond lengths	Atoms	Bond angles
C29–C30	1.412(13)	C19–C20–C15	118.3(7)
C31–O5	1.217(13)	C14–C20–C15	121.7(7)
C31–O1	1.302(12)	C22–C21–C29	118.8(8)
C31–C35	1.46(2)	C22–C21–C14	120.0(8)
C32–O6	1.184(12)	C29–C21–C14	121.1(8)
C32–O2	1.328(11)	C21–C22–O4	118.6(7)
C32–C36	1.509(14)	C21–C22–C23	123.3(9)
C33–O7	1.193(11)	O4–C22–C23	117.8(9)
C33–O3	1.364(11)	C24–C23–C22	117.3(10)
C33–C37	1.465(14)	C23–C24–C30	122.5(9)
C34–O8	1.183(10)	C26–C25–C30	122.4(12)
C34–O4	1.355(11)	C25–C26–C27	120.3(14)
C34–C38	1.447(14)	C28–C27–C26	121(2)
		C27–C28–C29	120.6(12)
		C21–C29–C30	119.5(10)
		C21–C29–C28	122.0(8)
		C30–C29–C28	118.3(10)
		C24–C30–C29	118.4(10)
		C24–C30–C25	123.8(10)
		C29–C30–C25	117.7(11)
		O5–C31–O1	122.8(11)
		O5–C31–C35	124.1(12)
		O1–C31–C35	112.9(11)
		O6–C32–O2	122.2(9)
		O6–C32–C36	126.6(11)
		O2–C32–C36	111.2(10)
		O7–C33–O3	120.2(8)
		O7–C33–C37	128.1(10)
		O3–C33–C37	111.7(10)
		O8–C34–O4	122.3(9)
		O8–C34–C38	125.8(10)
		O4–C34–C38	111.9(9)
		C31–O1–C2	119.0(7)
		C32–O2–C12	118.5(7)
		C33–O3–C13	118.0(7)
		C34–O4–C22	119.3(7)
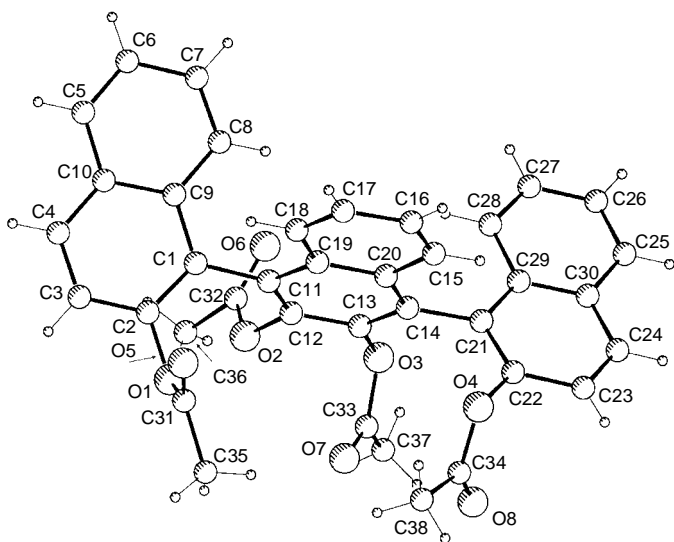
Fig. 1
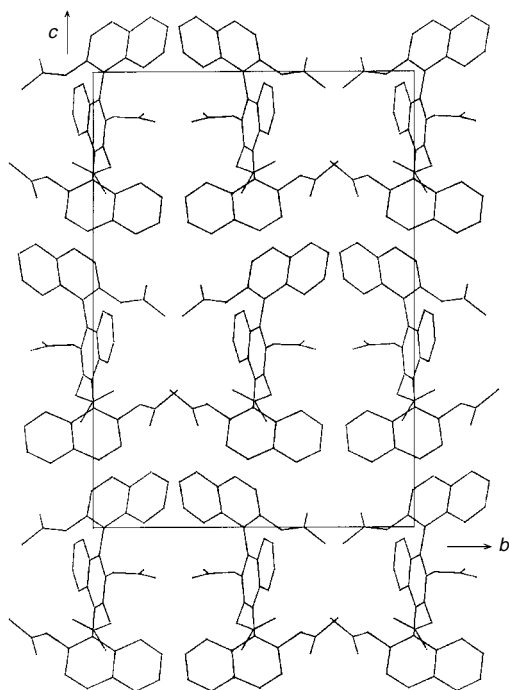Perspective view of the molecule with atom labelling

Fig. 2
Unit cell content viewed down the crystal-
lographic *a*-axis

90° being 6.0(6)° for the acetoxy group at C13. Obviously, this arrangement is intra-molecular in nature since the closest contacts between the molecules are at the van der Waals level.

REFERENCES

1. Belohradsky M., Budesinsky M., Gunterova J., Hodacova J., Holy P., Zavada J., Cisarova I., Podlaha J.: J. Org. Chem. *61*, 1205 (1996).
2. Sheldrick G. M.: Acta Crystallogr., A *46*, 467 (1990).
3. Sheldrick G. M.: *SHELXL93. Program for Crystal Structure Refinement from Diffraction Data*. University of Göttingen, Göttingen 1993.