Les structures ont été résolues avec le programme *MULTAN*77 (Main, Lessinger, Woolfson, Germain & Declercq, 1977) mais pour le composé (I), l'affinement était impossible à partir des positions obtenues. C'est pourquoi, le modèle a été translaté le long des axes de la maille en calculant pour chaque position le facteur R. La plus faible valeur du R trouvée ainsi, correspondait à une translation le long des axes [100] et [001] telle que x/a = 0,485 et z/c = 0,450, soit des translations respectivement de 8,019 Å et de 6,680 Å par rapport aux positions obtenues avec *MULTAN*77. Affinement des deux structures à l'aide d'une version modifiée de *ORFLS* (Busing, Martin & Levy, 1962). Pour les figures, utilisation du programme *ORTEP*II (Johnson, 1976). Ordinateur: IBM 3090 du CIRCE sous le système d'exploitation AIX/370

Les listes des facteurs de structure, des facteurs d'agitation thermique anisotrope, des coordonnées des atomes d'hydrogène et des distances et angles des atomes d'hydrogène ont été déposées aux dépôt d'archives de l'UICr (Référence: PA1097). On peut en obtenir des copies en s'adressant à: The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, Angleterre.

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2-Acetyl-1,8-dihydroxy-3,6-dimethylnaphthalene

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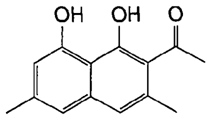
Abstract

The title compound, $C_{14}H_{14}O_3$, is essentially planar in the solid state with strictly intramolecular hydrogen bonds resembling those of acetylacetone.

Comment

2-Acetyl-1,8-dihydroxynaphthalene was found in the bark of the tree *Rhamnus frangula* (buckthorn) by Pailer, Jentzsch, Kump & Fuchs (1958). The molecule and its derivatives are potentially useful ligand systems. After twofold deprotonation they contain three O-atom donor centres arranged similarly to those in β,δ-triketones. In chelating coordination mode, they should be capable of ligation to two metal ions held in close spatial proximity by a rigid ligand system. Previous work has so far been limited to Co^{II}, Ni^{II} (Hynes & Walsh, 1987), Pd^{II} and Cu^{II} (Hoskins, McKenzie & Robson, 1992; Taguchi, Sagara, Kobayashi & Ueno, 1970). In the course of our investigations of the ligation properties of 2-acetyl-1,8-dihydroxynaphthalenes towards main group metals (Lutz, 1992), we determined the crystal and molecular structure of 2-acetyl-1,8-dihydroxy-3,6-dimethylnaphthalene (I).



(I)

The non-H atom skeleton of (I) is essentially planar in the solid state (Fig. 1). The coplanarity of the 2-acetyl residue undoubtedly has its origin in the intramolecular hydrogen bond formed between the acetyl O atom and the adjacent hydroxy group at C1. The other phenolic OH group (at C8) forms the second intramolecular hydrogen bond by acting as a hydrogen-bond donor for the hydroxy O atom at C1. The hydrogen bonds in (I) closely resemble those in acetylacetone (Camerman, Mastropaolo & Camerman, 1983) and its derivatives (Cradwick & Hall, 1971; Williams, 1966; Schlemper, 1982; Cea-Olivares, Rodriguez, Rosales & Toscano, 1987; Schaefer & Wheatley, 1966; Power, Turner & Moore, 1972; Power & Jones, 1971*a*,*b*,*c*,*d*). The crystal structure of (I) is characterized by parallel sheets of

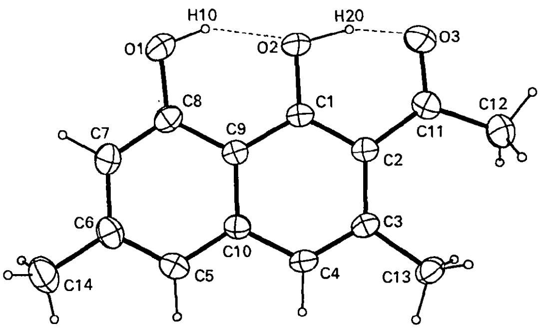


Fig. 1. Molecular structure of (I) and the crystallographic numbering scheme (*ORTEP*II; Johnson, 1976). Displacement ellipsoids are shown at the 50% level. For clarity, H atoms are drawn as spheres of arbitrary size.

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individual molecules (Fig. 2). Columns of molecules are arranged along the crystallographic *a* axis, the naphthalene skeletons of which are almost perfectly superimposed on one another. However, as a result of the intervening inversion centres the individual molecules adopt alternating orientations. In this way, no hydrophilic or hydrophobic domains are formed in the crystal structure.

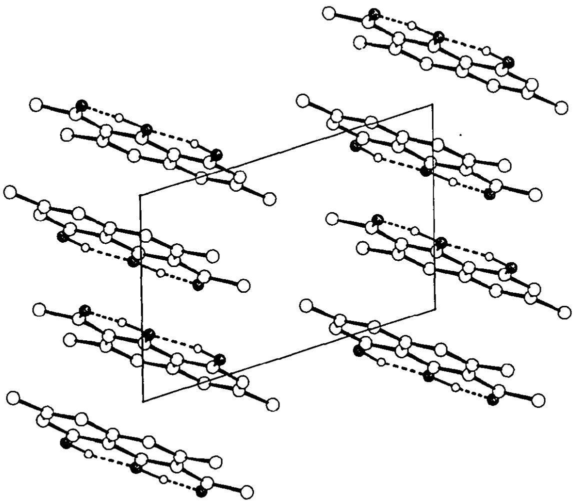

Fig. 2. Unit-cell contents of (I) as seen in projection down the *b* axis (*SCHAKAL92*; Keller, 1992). Shaded spheres are O atoms. H atoms have been omitted, except for those participating in hydrogen bonding.

Experimental

Compound (I) was synthesized following standard literature procedures (Bethell & Maitland, 1962; Overeem & van der Kerk, 1964). For purification, the compound was sublimed *in vacuo* at 423 K. Crystals suitable for X-ray structure determination were obtained by subsequent recrystallization from absolute ethanol.

Crystal data

$C_{14}H_{14}O_3$
$M_r = 230.25$
Triclinic
$P\bar{1}$
$a = 7.269$ (1) Å
$b = 7.517$ (1) Å
$c = 10.700$ (1) Å
$\alpha = 88.77$ (1)°
$\beta = 73.90$ (1)°
$\gamma = 76.20$ (1)°
$V = 544.9$ (1) Å^3
$Z = 2$
$D_x = 1.403$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 25 reflections
$\theta = 15.55$–$21.67°$
$\mu = 0.098$ mm^{-1}
$T = 215$ (2) K
Plate
0.3 × 0.3 × 0.1 mm
Yellow

Data collection

Enraf–Nonius CAD-4 four-circle diffractometer
$\omega/2\theta$ scans
Absorption correction: empirical
$T_{\min} = 0.93$, $T_{\max} = 1.00$
4992 measured reflections
2494 independent reflections
1851 observed reflections [$I > 2\sigma(I)$]

$R_{\text{int}} = 0.0145$
$\theta_{\max} = 27.44°$
$h = -9 \rightarrow 9$
$k = -9 \rightarrow 9$
$l = -13 \rightarrow 13$
3 standard reflections
frequency: 60 min
intensity variation: 0.3%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.0431$
$wR(F^2) = 0.1446$
$S = 1.040$
2494 reflections
210 parameters
All H-atom parameters refined
Calculated weights $w = 1/[\sigma^2(F_o^2) + (0.0924P)^2 + 0.0697P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.105$
$\Delta\rho_{\max} = 0.248$ e Å^{-3}
$\Delta\rho_{\min} = -0.290$ 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)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$$U_{\text{eq}} = (1/3)\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
O1	0.08420 (15)	0.22690 (13)	0.26192 (10)	0.0352 (3)
O2	0.31151 (14)	0.17657 (11)	0.02530 (9)	0.0323 (3)
O3	0.5229 (2)	0.12292 (12)	−0.19287 (10)	0.0388 (3)
C1	0.2776 (2)	0.3567 (2)	0.00836 (11)	0.0231 (3)
C2	0.3658 (2)	0.4263 (2)	−0.11163 (11)	0.0230 (3)
C3	0.3241 (2)	0.6231 (2)	−0.12258 (12)	0.0238 (3)
C4	0.2046 (2)	0.7333 (2)	−0.01798 (12)	0.0254 (3)
C5	−0.0055 (2)	0.7866 (2)	0.20885 (12)	0.0284 (3)
C6	−0.0904 (2)	0.7207 (2)	0.32626 (12)	0.0306 (3)
C7	−0.0583 (2)	0.5307 (2)	0.33980 (12)	0.0302 (3)
C8	0.0594 (2)	0.4079 (2)	0.23872 (12)	0.0259 (3)
C9	0.1503 (2)	0.47396 (15)	0.11669 (11)	0.0226 (3)
C10	0.1150 (2)	0.6657 (2)	0.10301 (11)	0.0238 (3)
C11	0.4930 (2)	0.2910 (2)	−0.21394 (12)	0.0275 (3)
C12	0.5968 (2)	0.3349 (2)	−0.34810 (14)	0.0375 (3)
C13	0.4053 (2)	0.7178 (2)	−0.24392 (13)	0.0318 (3)
C14	−0.2129 (3)	0.8508 (2)	0.4403 (2)	0.0446 (4)

Table 2. *Selected geometric parameters* (Å, °)

O1—C8	1.3560 (15)	C4—C10	1.421 (2)
O2—C1	1.3352 (14)	C5—C6	1.376 (2)
O3—C11	1.256 (2)	C5—C10	1.411 (2)
C1—C2	1.417 (2)	C6—C7	1.402 (2)
C1—C9	1.427 (2)	C6—C14	1.507 (2)
C2—C3	1.446 (2)	C7—C8	1.381 (2)
C2—C11	1.458 (2)	C8—C9	1.428 (2)
C3—C4	1.361 (2)	C9—C10	1.414 (2)
C3—C13	1.509 (2)	C11—C12	1.496 (2)
O2—C1—C2	121.03 (10)	C8—C7—C6	121.55 (12)
O2—C1—C9	116.77 (11)	O1—C8—C7	117.20 (11)
C2—C1—C9	122.20 (11)	O1—C8—C9	122.94 (11)
C1—C2—C3	118.02 (10)	C7—C8—C9	119.86 (11)
C1—C2—C11	116.41 (11)	C10—C9—C1	118.21 (11)
C3—C2—C11	125.57 (11)	C10—C9—C8	118.33 (11)
C4—C3—C2	119.18 (11)	C1—C9—C8	123.45 (11)
C4—C3—C13	116.51 (11)	C5—C10—C9	120.06 (11)
C2—C3—C13	124.31 (11)	C5—C10—C4	121.02 (11)
C3—C4—C10	123.46 (11)	C9—C10—C4	118.92 (10)
C6—C5—C10	120.87 (12)	O3—C11—C2	120.31 (11)
C5—C6—C7	119.32 (11)	O3—C11—C12	114.71 (11)
C5—C6—C14	120.52 (13)	C2—C11—C12	124.98 (11)
C7—C6—C14	120.15 (13)		

Table 3. *Hydrogen-bonding geometry* (Å, °)

D	H	*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1	H1O	O2	0.92 (2)	1.77 (2)	2.590 (1)	147 (2)
O2	H2O	O3	1.07 (3)	1.38 (3)	2.393 (1)	156 (2)

The structure was solved by direct methods in the non-centrosymmetric space group *P*1 but inspection of the atomic coordinates clearly showed the crystal structure to be centrosymmetric. All H-atom positions were found in difference syntheses. Data collection and cell refinement: Enraf–Nonius CAD-4 software. Data reduction: *MolEN* (Fair, 1990). Program used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ORTEP*II (Johnson, 1976); *SCHAKAL*92 (Keller, 1992). Software used to prepare material for publication: *SHELXL*93.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: SE1049). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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5,11,17,23-Tetra-*tert*-butyl-25,26,27,28-[(5-methylfurfuryl)oxycarbonylmethoxy]-calix[4]arene

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Abstract

The title molecule [tetrakis(5-methylfurfuryl) 5,11,17,23-tetra-*tert*-butylpentacyclo[19.3.1.1^{3,7}.1^{9,13}.1^{15,19}]-octacosa-1(25),3,5,7(28),9,11,13(27),15,17,19(26),21,23-dodecaene-25,26,27,28-tetrayltetraoxytetraacetate, $C_{76}H_{88}O_{16}$], which complexes Na^+ preferentially in solution, has twofold crystallographic symmetry and adopts a distorted cone conformation in the solid state. The orientation of the aromatic rings is such that two rings are almost parallel [interplanar angle 5.6 (1)°] and the other two are almost perpendicular to each other [interplanar angle 90.6 (1)°]. This conformation precludes any solvent molecule being enclathrated within the small molecular cavity.

Comment

The ability of calix[4]arene tetraesters of general formula (1) to form complexes with alkali metal cations is well established (Gutsche, 1989; Vicens & Böhmer, 1990). For the ethyl ester (2) there is a distinct preference for Na^+ over the other alkali cations as revealed by extraction studies and stability-constant measurements (Arnaud-Neu *et al.*, 1989). A study of substituent effects shows that changing the alkoxy moiety of the ester group can cause significant changes in complexation selectivities for Na^+ relative to K^+ (Arnaud-Neu *et al.*, 1992). One of the objectives of this research is to maximize complexation selectivities of chosen cations, for possible applications in sensors. Preliminary extraction studies with a new member of the tetraester series,