Crystal structure of 4,8-dihydroxy-1,5-bis(diphenylcarbamoyl)-*s*-indacene — dichloromethane (1:2), $C_{38}H_{26}N_2O_4 \cdot 2CH_2Cl_2$

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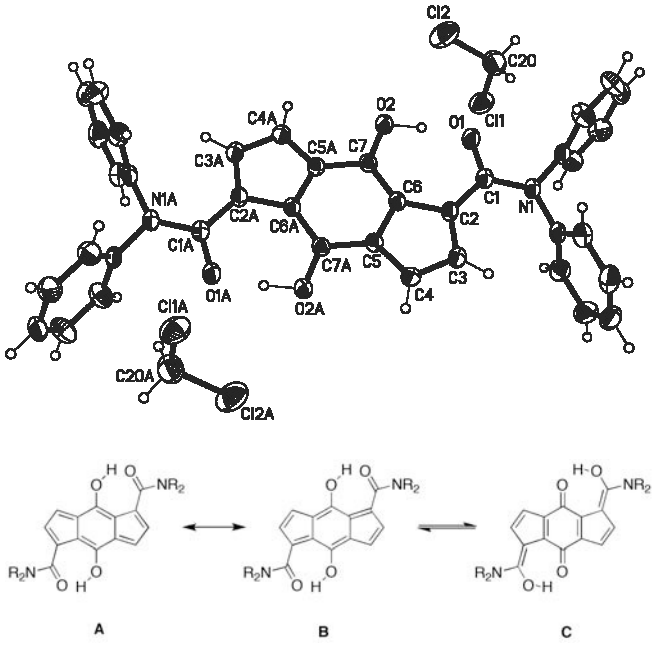

Abstract

$C_{40}H_{30}Cl_4N_2O_4$, triclinic, $P\bar{1}$ (no. 2), a = 9.3090(3) Å, b = 9.9510(4) Å, c = 10.3319(4) Å, α = 84.768(2)°, β = 73.098(2)°, γ = 70.600(2)°, V = 863.7 Å^3, Z = 1, $R_{gt}(F)$ = 0.038, $wR_{ref}(F^2)$ = 0.093, T = 233 K.

Source of material

The title compound was obtained by reaction of sodium cyclopentadienide with diphenylcarbamoyl chloride [1].

Experimental details

Hydrogen atoms attached to carbon atoms were calculated and refined using a riding model. Hydrogen atoms at oxygen atoms were refined free. The chlorine atoms of the solvent have a small position disorder with distances Cl1 to Cl1A of 24 pm and Cl2 to Cl2A of 52 pm. The ratio 4:1 was determined by varying the occupation of the major and minor positions to nearly equal values for the isotropic displacement parameters. For hydrogen calculation the carbon atom C20 was divided into C20 and C20A with equal coordinates and displacement parameters for both. The refinement of the major part without the disorder increases the R_{gt}(F) value from 0.038 to 0.052.

Discussion

In the asymmetric unit is a half molecule of a substituted *s*-indacene, which will be completed by a symmetry center, and a solvent molecule of dichloromethane, showing a 4 : 1 position disorder of the chlorine atoms. The bonding situation in this molecule can be described *via* two mesomeric forms A and B and the tautomeric form C by movement of the hydrogen position between the oxygen atoms. Our interest in this structure was the symmetry of the O–H–O hydrogen bond, which we have extensively discussed for a related system [2]. An analysis of the bond lengths leads to a mixture between form A and C with a major amount of A. The distance C7—O2 of 131.0(2) pm is too short for an enolic bond, and the distance C1—O1 of 126.2(2) pm too long for the bond length of an amide group. These bond lengths are given in the literature [3] with 133.3 and 123.4 pm, respectively. The O1···O2 distance of 245.6(2) pm is short and can favor a tautomerism. The hydrogen atom at O2 was localized and refined with an isotropic displacement parameter. Here we have an asymmetric O–H–O bond with a distance of 105(3) pm to O2 and 141(3) pm to O1, thereby showing a tautomeric equilibrium in the solid state. The distances C1—C2, C2—C6, C6—C5 and C5—C7A of 146.1(2), 145.8(2), 142.7(2) and 144.2(2) pm are in the range of conjugated single bonds, whereas the distances C2—C3, C4—C5 and C6—C7 of 140.1(2), 138.3(2) and 139.9(2) pm are more in the range of double bonds. This distribution of carbon bond lengths shows that the structure of the indacene is mainly dominated by the form A in the scheme.

Table 1. Data collection and handling.

Crystal:	brown prism, size 0.07 × 0.1 × 0.3 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	3.89 cm^{-1}
Diffractometer, scan mode:	Nonius Kappa CCD, φ/ω
$2\theta_{max}$:	50°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	5252, 2971
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 2609
$N(param)_{refined}$:	249
Programs:	SHELXS-97 [4], SHELXL-97 [5], SHELXTL [6]

Table 2. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	Occ.	x	y	z	U_{iso}
H(2O)	2*i*		–0.275(3)	0.317(3)	0.689(2)	0.072(7)
H(3)	2*i*		–0.0312	0.3558	0.2220	0.043
H(4)	2*i*		–0.2831	0.5003	0.1677	0.040
H(9)	2*i*		0.1835	0.0445	0.2463	0.047
H(10)	2*i*		0.3316	0.0597	0.0252	0.057

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Table 2. Continued.

Atom	Site	Occ.	x	y	z	U_{iso}
H(11)	2*i*		0.4307	0.2480	–0.0403	0.061
H(12)	2*i*		0.3813	0.4227	0.1147	0.061
H(13)	2*i*		0.2281	0.4118	0.3359	0.049
H(15)	2*i*		0.1579	–0.0472	0.5269	0.053
H(16)	2*i*		0.3178	–0.1749	0.6617	0.062
H(17)	2*i*		0.4502	–0.0651	0.7521	0.053

Table 2. Continued.

Atom	Site	Occ.	x	y	z	U_{iso}
H(18)	2*i*		0.4242	0.1726	0.7079	0.057
H(19)	2*i*		0.2624	0.3022	0.5747	0.050
H(20A)	2*i*	0.80	0.0432	0.1257	0.9673	0.069
H(20B)	2*i*	0.80	0.0198	0.1533	0.8201	0.069
H(20C)	2*i*	0.20	0.0684	0.1289	0.9449	0.069
H(20D)	2*i*	0.20	–0.0057	0.1597	0.8211	0.069

Table 3. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	Occ.	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
N(1)	2*i*		0.1008(2)	0.2182(1)	0.4499(1)	0.0218(7)	0.0342(7)	0.0340(7)	–0.0050(6)	–0.0078(6)	0.0004(6)
O(1)	2*i*		–0.1113(1)	0.2533(1)	0.6272(1)	0.0254(6)	0.0542(8)	0.0323(7)	–0.0042(5)	–0.0087(5)	0.0064(5)
O(2)	2*i*		–0.3982(1)	0.3683(1)	0.7183(1)	0.0262(6)	0.0481(7)	0.0307(6)	–0.0049(5)	–0.0089(5)	0.0079(5)
C(1)	2*i*		–0.0576(2)	0.2750(2)	0.5030(2)	0.0244(8)	0.0306(8)	0.0343(9)	–0.0065(7)	–0.0078(7)	–0.0015(7)
C(2)	2*i*		–0.1642(2)	0.3569(2)	0.4236(2)	0.0221(8)	0.0293(8)	0.0332(9)	–0.0062(6)	–0.0068(7)	0.0002(6)
C(3)	2*i*		–0.1318(2)	0.3860(2)	0.2848(2)	0.0252(9)	0.043(1)	0.0318(9)	–0.0054(7)	–0.0044(7)	0.0022(7)
C(4)	2*i*		–0.2736(2)	0.4675(2)	0.2540(2)	0.0293(9)	0.0409(9)	0.0282(8)	–0.0083(7)	–0.0086(7)	0.0048(7)
C(5)	2*i*		–0.3962(2)	0.4911(2)	0.3721(2)	0.0247(8)	0.0282(8)	0.0297(8)	–0.0083(6)	–0.0083(7)	0.0011(6)
C(6)	2*i*		–0.3343(2)	0.4229(2)	0.4810(2)	0.0226(8)	0.0258(8)	0.0306(8)	–0.0067(6)	–0.0087(7)	0.0000(6)
C(7)	2*i*		–0.4386(2)	0.4295(2)	0.6106(2)	0.0256(8)	0.0270(8)	0.0296(8)	–0.0086(6)	–0.0105(7)	0.0020(6)
C(8)	2*i*		0.1901(2)	0.2285(2)	0.3112(2)	0.0202(8)	0.0361(9)	0.0347(9)	–0.0034(7)	–0.0090(7)	0.0007(7)
C(9)	2*i*		0.2220(2)	0.1218(2)	0.2195(2)	0.0306(9)	0.040(1)	0.045(1)	–0.0065(8)	–0.0115(8)	–0.0047(8)
C(10)	2*i*		0.3110(2)	0.1307(2)	0.0885(2)	0.035(1)	0.058(1)	0.041(1)	–0.0014(9)	–0.0104(9)	–0.0120(9)
C(11)	2*i*		0.3701(2)	0.2429(2)	0.0492(2)	0.033(1)	0.074(1)	0.037(1)	–0.010(1)	–0.0057(8)	0.005(1)
C(12)	2*i*		0.3402(2)	0.3469(2)	0.1411(2)	0.043(1)	0.059(1)	0.051(1)	–0.022(1)	–0.0099(9)	0.012(1)
C(13)	2*i*		0.2492(2)	0.3403(2)	0.2730(2)	0.037(1)	0.042(1)	0.044(1)	–0.0134(8)	–0.0109(8)	0.0010(8)
C(14)	2*i*		0.1963(2)	0.1394(2)	0.5379(2)	0.0202(8)	0.0345(9)	0.0328(9)	–0.0042(7)	–0.0067(7)	–0.0015(7)
C(15)	2*i*		0.2117(2)	–0.0025(2)	0.5636(2)	0.048(1)	0.036(1)	0.057(1)	–0.0127(8)	–0.027(1)	0.0011(8)
C(16)	2*i*		0.3069(3)	–0.0782(2)	0.6438(2)	0.059(1)	0.034(1)	0.061(1)	–0.0044(9)	–0.027(1)	0.0049(9)
C(17)	2*i*		0.3856(2)	–0.0131(2)	0.6975(2)	0.0303(9)	0.055(1)	0.041(1)	–0.0024(8)	–0.0152(8)	0.0045(9)
C(18)	2*i*		0.3699(2)	0.1281(2)	0.6715(2)	0.043(1)	0.063(1)	0.049(1)	–0.025(1)	–0.0233(9)	0.0070(9)
C(19)	2*i*		0.2740(2)	0.2052(2)	0.5918(2)	0.043(1)	0.041(1)	0.048(1)	–0.0187(8)	–0.0183(9)	0.0050(8)
C(20)	2*i*	0.80	–0.0209(3)	0.1905(2)	0.9129(2)	0.051(1)	0.051(1)	0.070(2)	–0.015(1)	–0.020(1)	0.005(1)
Cl(1)	2*i*	0.80	–0.0016(2)	0.3593(1)	0.9133(1)	0.0600(5)	0.0484(5)	0.0593(6)	–0.0277(4)	–0.0027(5)	–0.0008(4)
Cl(2)	2*i*	0.80	–0.2201(3)	0.1948(3)	0.9785(2)	0.0630(7)	0.102(1)	0.0696(8)	–0.0500(7)	–0.0115(5)	0.0101(6)
C(20A)	2*i*	0.20	–0.0209(3)	0.1905(2)	0.9129(2)	0.051(1)	0.051(1)	0.070(2)	–0.015(1)	–0.020(1)	0.005(1)
Cl(2A)	2*i*	0.20	–0.187(1)	0.171(1)	1.012(1)	0.111(7)	0.084(5)	0.111(7)	–0.058(5)	0.028(4)	–0.027(5)
Cl(1A)	2*i*	0.20	–0.020(2)	0.350(1)	0.908(1)	0.20(1)	0.146(7)	0.153(8)	–0.121(7)	0.029(7)	–0.055(6)

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