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Crystal structure of methyl (1-phenylethyl) carbamate, $C_{10}H_{13}NO_2$

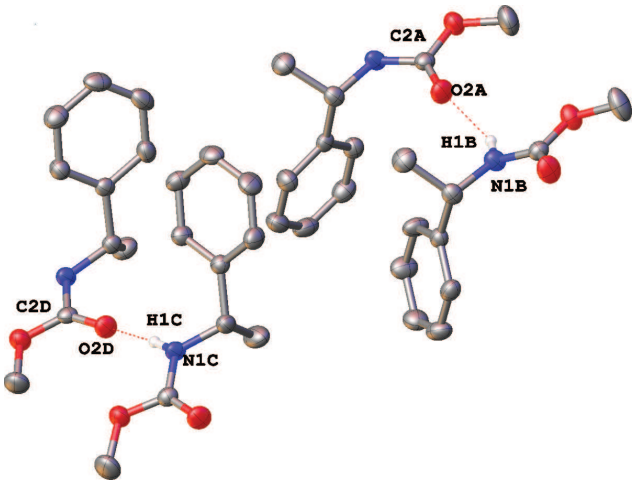

Table 1: Data collection and handling.

Crystal:	Colorless block
Size:	0.28 × 0.27 × 0.09 mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ:	0.08 mm^{-1}
Diffractometer, scan mode:	Bruker Kappa Duo Apex II, 0.5 φ and ω-scans
θ_{max}, completeness:	28.4°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	22398, 5260, 0.043
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 4403
$N(param)_{refined}$:	493
Programs:	Bruker programs [1], SHELX [2], OLEX2 [3]

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Abstract

$C_{10}H_{13}NO_2$, monoclinic, $P2_1$ (no. 14), $a = 9.9882(7)$ Å, $b = 8.5202(6)$ Å, $c = 23.1403(18)$ Å, $\beta = 91.010(2)°$, $V = 1969.0(2)$ Å^3, $Z = 8$, $R_{gt}(F) = 0.0387$, $wR_{ref}(F^2) = 0.0919$, $T = 173(2)$K.

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The asymmetric unit of the title crystal structure is shown in the figure. Tables 1 and 2 contain details on crystal structure and measurement conditions and a list of the atoms including atomic coordinates and displacement parameters.

Source of material

The resorcarene (0.125 mmol), which was isolated by column chromatography, was dissolved in anhydrous methanol (3 mL), and a freshly prepared sodium methoxide solution (1 M, 100 µL) was added. The reaction mixture was stirred at room temperature for 2–3 h and then neutralized with Amberlite IRC-50H resin. The resin was removed by filtration through a glass wool plug and was washed with ethyl acetate. The solvent was removed under reduced pressure, and the crude product was purified by column chromatography (eluted with hexane/EtOAc (60:10 to 60:40) to yield enantiomerically pure tetramethoxyresorcarenes. We obtained methyl 1-phenylethylcarbamate as colorless crystals (10% yield) M.p. = 333–335 K. Crystals suitable for X-ray diffraction were obtained by slow evaporation of the hexane/EtOAc (60:10) solvent fraction at room temperature.

Experimental details

All hydrogen atoms, except the amino hydrogen atoms, were placed in idealised positions and refined in riding models with U_{iso} assigned the values to be 1.2 or 1.5 times those of their parent atoms and the constraint distances of C—H ranging from 0.95 Å to 1.00 Å. The amino hydrogen atoms were located in the difference electron density maps and refined without any restraints.

Discussion

Carbamates like the title compound are generally prepared from phosgene, phosgene derivatives or isocyanates [4, 5]. Such chiral amine synthons have been used for the construction of pharmaceuticals and natural products. In particular, cyclic derivatives of these chiral synthons have been used in the construction of peptidomimetics.

Protection of organic functions plays a fundamental role in the field of multi-step organic synthesis [6]. Amine

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Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2).

Atom	*x*	*y*	*z*	U_{iso}*/U_{eq}
O1A	0.60629(15)	1.10819(19)	0.95547(7)	0.0377(4)
O2A	0.44376(13)	0.98681(19)	0.90310(7)	0.0383(4)
N1A	0.66202(17)	0.9735(2)	0.87845(8)	0.0298(4)
H1A	0.738(2)	0.999(3)	0.8882(10)	0.032(6)*
C1A	0.5056(3)	1.1659(4)	0.99337(12)	0.0537(7)
H1A1	0.4423	1.2318	0.9715	0.081*
H1A2	0.5480	1.2282	1.0242	0.081*
H1A3	0.4577	1.0772	1.0103	0.081*
C2A	0.56111(19)	1.0192(2)	0.91123(9)	0.0272(4)
C3A	0.6450(2)	0.8765(2)	0.82735(9)	0.0279(4)
H3A	0.5490	0.8830	0.8146	0.033*
C4A	0.7303(2)	0.9453(3)	0.77927(10)	0.0379(5)
H4A1	0.7014	1.0530	0.7711	0.057*
H4A2	0.7195	0.8814	0.7443	0.057*
H4A3	0.8247	0.9455	0.7916	0.057*
C5A	0.67765(19)	0.7044(2)	0.83888(9)	0.0262(4)
C6A	0.7199(2)	0.6507(3)	0.89245(9)	0.0311(5)
H6A	0.7290	0.7224	0.9237	0.037*
C7A	0.7494(2)	0.4925(3)	0.90126(10)	0.0386(5)
H7A	0.7772	0.4571	0.9385	0.046*
C8A	0.7384(2)	0.3877(3)	0.85652(12)	0.0421(6)
H8A	0.7605	0.2804	0.8623	0.051*
C9A	0.6949(2)	0.4397(3)	0.80298(11)	0.0416(6)
H9A	0.6858	0.3673	0.7719	0.050*
C10A	0.6645(2)	0.5960(3)	0.79413(10)	0.0359(5)
H10A	0.6342	0.6300	0.7570	0.043*
O1B	0.09585(14)	1.08211(18)	0.96694(7)	0.0363(4)
O2B	−0.05797(14)	1.0114(2)	0.89966(7)	0.0442(4)
N1B	0.15492(18)	0.9229(2)	0.89644(8)	0.0298(4)
H1B	0.230(3)	0.942(3)	0.9106(12)	0.052(8)*
C1B	−0.0048(3)	1.1743(4)	0.99480(13)	0.0548(7)
H1B1	−0.0349	1.2584	0.9688	0.082*
H1B2	0.0329	1.2203	1.0303	0.082*
H1B3	−0.0810	1.1072	1.0043	0.082*
C2B	0.05556(19)	1.0054(2)	0.91884(9)	0.0268(4)
C3B	0.1386(2)	0.8344(2)	0.84268(9)	0.0289(4)
H3B	0.0411	0.8351	0.8320	0.035*
C4B	0.2129(2)	0.9146(3)	0.79409(10)	0.0394(5)
H4B1	0.1772	1.0206	0.7883	0.059*
H4B2	0.2011	0.8539	0.7584	0.059*
H4B3	0.3085	0.9208	0.8042	0.059*
C5B	0.1802(2)	0.6645(2)	0.85115(9)	0.0272(4)
C6B	0.0860(2)	0.5460(3)	0.84920(9)	0.0331(5)
H6B	−0.0055	0.5715	0.8422	0.040*
C7B	0.1225(3)	0.3905(3)	0.85723(11)	0.0411(6)
H7B	0.0562	0.3106	0.8560	0.049*
C8B	0.2543(3)	0.3516(3)	0.86688(11)	0.0417(6)
H8B	0.2797	0.2450	0.8720	0.050*
C9B	0.3495(2)	0.4685(3)	0.86909(11)	0.0430(6)
H9B	0.4408	0.4422	0.8760	0.052*
C10B	0.3131(2)	0.6243(3)	0.86134(11)	0.0372(5)
H10B	0.3796	0.7040	0.8630	0.045*
O1C	0.38607(14)	0.03322(18)	0.54082(6)	0.0352(3)
O2C	0.20286(14)	0.1213(2)	0.58636(7)	0.0400(4)
N1C	0.40982(18)	0.2200(2)	0.60562(8)	0.0291(4)
H1C	0.489(2)	0.207(3)	0.6017(10)	0.029(6)*
C1C	0.3055(3)	−0.0822(3)	0.51168(12)	0.0530(7)
H1C1	0.2619	−0.1489	0.5403	0.080*
H1C2	0.3624	−0.1470	0.4871	0.080*
H1C3	0.2372	−0.0298	0.4877	0.080*
C2C	0.32299(19)	0.1245(2)	0.57879(9)	0.0268(4)
C3C	0.3727(2)	0.3192(2)	0.65363(10)	0.0311(5)
H3C	0.2729	0.3291	0.6525	0.037*
C4C	0.4114(3)	0.2426(3)	0.71083(11)	0.0512(7)
H4C1	0.3670	0.1403	0.7137	0.077*
H4C2	0.3833	0.3099	0.7427	0.077*
H4C3	0.5087	0.2281	0.7129	0.077*
C5C	0.43006(19)	0.4834(2)	0.64871(9)	0.0266(4)
C6C	0.5627(2)	0.5082(2)	0.63401(9)	0.0309(4)
H6C	0.6191	0.4212	0.6263	0.037*
C7C	0.6133(2)	0.6598(3)	0.63053(10)	0.0355(5)
H7C	0.7039	0.6757	0.6202	0.043*
C8C	0.5333(2)	0.7868(3)	0.64198(10)	0.0367(5)
H8C	0.5682	0.8903	0.6395	0.044*
C9C	0.4016(3)	0.7626(3)	0.65722(12)	0.0424(6)
H9C	0.3458	0.8498	0.6656	0.051*
C10C	0.3509(2)	0.6118(3)	0.66035(10)	0.0368(5)
H10C	0.2602	0.5964	0.6707	0.044*
O1D	0.83908(14)	0.03316(18)	0.53816(7)	0.0350(3)
O2D	0.69544(13)	0.14204(18)	0.60124(7)	0.0350(4)
N1D	0.91922(17)	0.1796(2)	0.60927(8)	0.0289(4)
H1D	0.993(2)	0.156(3)	0.5961(9)	0.028(6)*
C1D	0.7278(2)	−0.0397(3)	0.50809(11)	0.0444(6)
H1D1	0.6843	−0.1146	0.5339	0.067*
H1D2	0.7603	−0.0952	0.4740	0.067*
H1D3	0.6633	0.0410	0.4960	0.067*
C2D	0.80904(19)	0.1205(2)	0.58448(9)	0.0250(4)
C3D	0.9162(2)	0.2770(2)	0.66051(9)	0.0273(4)
H3D	0.8220	0.2765	0.6744	0.033*
C4D	1.0034(2)	0.2041(3)	0.70809(10)	0.0399(5)
H4D1	0.9678	0.1007	0.7182	0.060*
H4D2	1.0031	0.2720	0.7423	0.060*
H4D3	1.0952	0.1928	0.6945	0.060*
C5D	0.95261(18)	0.4468(2)	0.64811(9)	0.0259(4)
C6D	0.9849(2)	0.4992(2)	0.59351(9)	0.0316(5)
H6D	0.9876	0.4269	0.5623	0.038*
C7D	1.0136(2)	0.6574(3)	0.58386(11)	0.0406(5)
H7D	1.0348	0.6920	0.5461	0.049*
C8D	1.0112(2)	0.7638(2)	0.62885(12)	0.0409(6)
H8D	1.0314	0.8712	0.6223	0.049*
C9D	0.9795(2)	0.7123(3)	0.68291(12)	0.0401(6)
H9D	0.9772	0.7851	0.7140	0.048*
C10D	0.9508(2)	0.5556(3)	0.69308(10)	0.0341(5)
H10D	0.9296	0.5221	0.7310	0.041*

functions are found in a great number of biologically active compounds, making their protection an important question in synthetic and medicinal chemistry [7]. Many methods have been employed to protect this group. The *N*-methyloxycarbonylation has been applied due to ease of addition and removal. The methyloxy group is very stable

in a wide range of synthetic conditions. The structures of these protected compounds have been rarely reported [6–9].

For the preparation of enantiomerically pure C_4-symmetric tetramethoxy-resorcarenes we synthesized tetramethoxy-resorcarenecarbamate derivatives by reacting tetramethoxy-resorcarenes with (*S*)-(-)-1-phenylethyl isocyanate [10]. We obtained methyl 1-phenylethylcarbamate as one by-product during the hydrolysis step while obtaining the desired enantiomerically pure tetramethoxy-resorcarenes [10].

There are four crystallographically independent molecules in the asymmetric unit. Each of these four molecules has as its fundamental moiety a carbamate functional group (*cf*. the figure). The molecules are aligned *via* N—H···O hydrogen bonding interactions. This connects two crystallographically independent molecules creating two chains along the [010] axis and a layered structure across the *ac* plane.

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