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2-[(1*E*,4*E*)-4-(2-Methoxyphenyl)-3*H*-benzo[*b*][1,5]diazepin-2-yl]phenol

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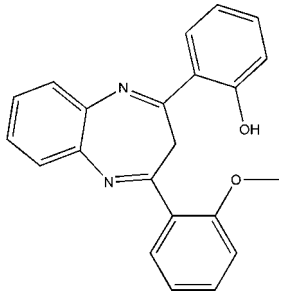
Key indicators: single-crystal X-ray study; T = 298 K; mean σ(C–C) = 0.002 Å; R factor = 0.041; wR factor = 0.120; data-to-parameter ratio = 17.5.

The asymmetric unit of the title compound, $C_{22}H_{18}N_2O_2$, contains two crystallographically independent molecules, in which each molecule is composed of three planar six-membered rings and one nonplanar seven-membered ring. The six-membered *A* (phenol), *B* (fused benzene) and *C* (methoxyphenyl) rings are oriented with respect to each other at dihedral angles of 88.79 (3) (*A*/*B*), 68.16 (3) (*A*/*C*) and 37.51 (2)° (*B*/*C*), and 82.43 (3) (*A*′/*B*′), 78.52 (2) (*A*′/*C*′) and 28.65 (3)° (*B*′/*C*′). The seven-membered rings adopt near-boat conformations. Intramolecular O—H···N and C—H···O hydrogen bonds are present in the crystal structure.

Related literature

For bond-length data, see: Allen (2002); Bruno *et al.* (2004). For general background, see: Krapcho & Turk (1966); Gringauz (1999); Butcher & Hamor (1985); Armarego (1977). For related literature, see: Ahmed *et al.* (1990).



Experimental

Crystal data

$C_{22}H_{18}N_2O_2$
M_r = 342.38
Monoclinic, $P2_1/c$
a = 14.3963 (6) Å
b = 19.0230 (8) Å
c = 12.7651 (6) Å
β = 91.305 (1)°
V = 3495.0 (3) Å^3
Z = 8
Mo $K\alpha$ radiation
μ = 0.08 mm^{-1}
T = 298 (2) K
0.32 × 0.28 × 0.26 mm

Data collection

Bruker SMART CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.924, T_{max} = 0.977
21496 measured reflections
8356 independent reflections
5640 reflections with $I > 2\sigma(I)$
R_{int} = 0.021

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.042
$wR(F^2)$ = 0.120
S = 1.00
8356 reflections
477 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.17 e Å^{-3}
$\Delta\rho_{min}$ = −0.19 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O2—H2···N2	0.95 (2)	1.69 (2)	2.5749 (18)	154 (2)
O3—H3···N4	0.97 (2)	1.71 (2)	2.5921 (16)	150.6 (18)
C9—H9*B*···O1	0.97	2.42	2.8971 (17)	110
C31—H31*B*···O4	0.97	2.25	2.8830 (18)	122

Data collection: *SMART* (Bruker, 1998); cell refinement: *SAINT* (Bruker, 1999); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 1999); software used to prepare material for publication: *SHELXTL*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HK2294).

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supplementary materials

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2-[(1*E*,4*E*)-4-(2-Methoxyphenyl)-3*H*-benzo[*b*][1,5]diazepin-2-yl]phenol

M. Zia-ul-Haq, A. Munir, G. Qadeer, N. H. Rama and W.-Y. Wong

Comment

The title compound belongs to an important class of the pharmacologically pre-eminent 1,5-benzodiazepines which are extensively studied for medicinal activities (Krapcho & Turk, 1966). In recent years, benzodiazepines have replaced barbiturates which were used once for the purpose of hypnotic effects, owing to their less toxic and less severe withdrawal effects (Gringauz, 1999). The importance of 1,5-benzodiazepines, in particular is evident from the pharmaceutical application of Globazam (Butcher & Hamor, 1985). The difficulties encountered in the cyclization of these seven-membered heterocycles limited their structural studies. In view of the importance of this class of compounds, the title compound, (I), has been synthesized and its crystal structure is reported here.

The asymmetric unit of the title compound, (I), contains two crystallographicaly independent molecules (Fig. 1). Bond lengths and angles can be regarded as normal (Cambridge Structural Database, Version 5.28, November 2006; Allen, 2002; Mogul, Version 1.1; Bruno *et al.*, 2004). The seven membered diazepine rings have fragments N1—C12—C11—N2 and N3—C34—C33—N4, which are conjugated with the adjacent benzene rings. Like azepines, diazepines are not planar and generally adopt boat conformation (Armarego, 1977).

The rings A (C2—C7), B (C11—C16), C (C17—C22) and A' (C24—C29), B' (C33—C38), C' (C39—C44) are, of course, planar and dihedral angles between them are A/B = 88.79 (3)°, A/C = 68.16 (3)°, B/C = 37.51 (2)° and A'/B' = 82.43 (3)°, A'/C' = 78.52 (2)°, B'/C' = 28.65 (3)°. The seven membered rings D (N1/N2/C8—C12) and D' (N3/N4/C30—C34) are not planar and adopt nearly boat conformations.

The intramolecular O—H···N and C—H···O hydrogen bonds (Table 1) may be effective in the stabilization of the structure.

Experimental

1-(2-hydroxyphenyl)-3-(2-methoxyphenyl)propane-1,3-dione (2.7 g, 10 mmol), prepared according to the reported procedure (Ahmed *et al.*, 1990), was subjected to *cyclo*-condensation with phenylene diamine (1,08 g, 10 mmol) using toluene as solvent (100 ml) to get the title compound (yield; 69%, m.p. 439–440 K). Yellow single crystals suitable for X-ray analysis were obtained by slow evaporation of dichloromethane solution.

Refinement

H2 and H3 (for OH groups) were located in difference syntheses and refined isotropically [O2—H2 = 0.95 (2) Å, U_{iso}(H) = 0.098 (7) Å^2 and O3—H3 = 0.97 (2) Å, U_{iso}(H) = 0.093 (7) Å^2]. The remaining H atoms were positioned geometrically, with C—H = 0.93, 0.97 and 0.96 Å for aromatic, methylene and methyl H atoms, and constrained to ride on their parent atoms, with U_{iso}(H) = xU_{eq}(C), where x = 1.5 for methyl H, and x = 1.2 for all other H atoms.

Figures

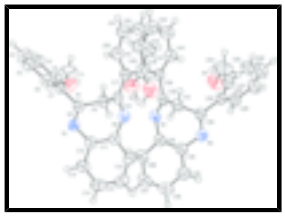


Fig. 1. The molecular structure of the title molecule, with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

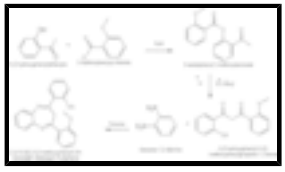


Fig. 2. The formation of the title compound.

2-[(1E,4E)-4-(2-Methoxyphenyl)-3*H*-benzo[*b*][1,5]diazepin-2-yl]phenol

Crystal data

$C_{22}H_{18}N_2O_2$	F_{000} = 1440
M_r = 342.38	D_x = 1.301 Mg m^{-3}
Monoclinic, $P2_1/c$	Melting point: 439(1) K
Hall symbol: -P 2ybc	Mo $K\alpha$ radiation λ = 0.71073 Å
a = 14.3963 (6) Å	Cell parameters from 2164 reflections
b = 19.0230 (8) Å	θ = 2.1–27.5º
c = 12.7651 (6) Å	μ = 0.08 mm^{-1}
β = 91.305 (1)º	T = 298 (2) K
V = 3495.0 (3) Å^3	Block, yellow
Z = 8	0.32 × 0.28 × 0.26 mm

Data collection

Bruker SMART CCD area-detector diffractometer	8356 independent reflections
Radiation source: fine-focus sealed tube	5640 reflections with $I > 2\sigma(I)$
Monochromator: graphite	R_{int} = 0.021
T = 298(2) K	θ_{max} = 28.3º
ω and φ scans	θ_{min} = 2.4º
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)	h = −18→19
T_{min} = 0.924, T_{max} = 0.977	k = −21→24
21496 measured reflections	l = −9→16

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.042$

$wR(F^2) = 0.120$

$S = 1.00$

8356 reflections

477 parameters

Primary atom site location: structure-invariant direct methods

Hydrogen site location: inferred from neighbouring sites

H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0559P)^2 + 0.4964P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} < 0.001$

$\Delta\rho_{max} = 0.17$ e Å^{-3}

$\Delta\rho_{min} = -0.19$ e Å^{-3}

Extinction correction: none

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted *R*-factor *wR* and goodness of fit S are based on F^2, conventional *R*-factors *R* are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2$sigma(F^2) is used only for calculating *R*-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on F, and R– factors based on ALL data will be even larger.

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

	x	*y*	*z*	U_{iso}*/U_{eq}
O1	−0.03830 (7)	0.34099 (6)	0.70821 (9)	0.0648 (3)
O2	0.41848 (8)	0.44392 (7)	0.86472 (11)	0.0692 (3)
H2	0.4019 (15)	0.4151 (11)	0.8062 (18)	0.098 (7)*
O3	0.02097 (8)	0.52556 (7)	0.61006 (10)	0.0640 (3)
H3	0.0736 (15)	0.5167 (11)	0.5662 (16)	0.093 (7)*
O4	0.43830 (8)	0.65133 (7)	0.77294 (10)	0.0718 (3)
N1	0.19680 (7)	0.25092 (6)	0.69141 (9)	0.0428 (3)
N2	0.32563 (8)	0.37444 (6)	0.72447 (9)	0.0443 (3)
N3	0.35974 (8)	0.60184 (6)	0.48265 (10)	0.0474 (3)
N4	0.18993 (7)	0.52098 (5)	0.54442 (9)	0.0420 (3)
C1	−0.12668 (13)	0.37289 (13)	0.69734 (18)	0.0980 (7)
H1A	−0.1286	0.4016	0.6355	0.147*
H1B	−0.1379	0.4016	0.7576	0.147*
H1C	−0.1736	0.3371	0.6916	0.147*
C2	−0.02081 (9)	0.29743 (7)	0.79152 (11)	0.0461 (3)
C3	−0.08829 (10)	0.27298 (9)	0.85813 (13)	0.0585 (4)
H3A	−0.1497	0.2874	0.8489	0.070*
C4	−0.06431 (12)	0.22745 (9)	0.93786 (13)	0.0616 (4)
H4A	−0.1099	0.2115	0.9825	0.074*
C5	0.02575 (12)	0.20512 (8)	0.95271 (12)	0.0578 (4)
H5A	0.0414	0.1747	1.0074	0.069*

C6	0.09268 (10)	0.22841 (7)	0.88528 (11)	0.0477 (3)
H6A	0.1535	0.2127	0.8943	0.057*
C7	0.07119 (9)	0.27470 (6)	0.80432 (10)	0.0398 (3)
C8	0.14392 (8)	0.29780 (7)	0.73142 (10)	0.0396 (3)
C9	0.15782 (9)	0.37523 (7)	0.71038 (11)	0.0433 (3)
H9A	0.1612	0.3841	0.6357	0.052*
H9B	0.1071	0.4025	0.7382	0.052*
C10	0.24804 (9)	0.39396 (6)	0.76502 (11)	0.0417 (3)
C11	0.32698 (9)	0.32981 (7)	0.63671 (10)	0.0419 (3)
C12	0.26806 (8)	0.27080 (7)	0.62375 (10)	0.0410 (3)
C13	0.28398 (10)	0.22507 (8)	0.53994 (12)	0.0508 (3)
H13A	0.2489	0.1842	0.5336	0.061*
C14	0.35000 (10)	0.23924 (9)	0.46712 (12)	0.0578 (4)
H14A	0.3571	0.2096	0.4100	0.069*
C15	0.40615 (10)	0.29817 (9)	0.47921 (12)	0.0574 (4)
H15A	0.4503	0.3084	0.4294	0.069*
C16	0.39664 (9)	0.34117 (8)	0.56410 (12)	0.0503 (3)
H16A	0.4373	0.3787	0.5737	0.060*
C17	0.25098 (10)	0.43259 (7)	0.86479 (11)	0.0462 (3)
C18	0.33617 (11)	0.45524 (8)	0.91028 (13)	0.0543 (4)
C19	0.33710 (14)	0.49073 (9)	1.00579 (14)	0.0688 (5)
H19A	0.3932	0.5064	1.0349	0.083*
C20	0.25624 (16)	0.50274 (9)	1.05710 (15)	0.0743 (5)
H20A	0.2580	0.5261	1.1211	0.089*
C21	0.17215 (15)	0.48061 (9)	1.01487 (14)	0.0705 (5)
H21A	0.1174	0.4888	1.0502	0.085*
C22	0.16991 (12)	0.44620 (8)	0.91974 (13)	0.0578 (4)
H22A	0.1130	0.4317	0.8914	0.069*
C23	0.49355 (14)	0.66690 (13)	0.86386 (16)	0.0896 (7)
H23A	0.5130	0.6239	0.8969	0.134*
H23B	0.4577	0.6940	0.9118	0.134*
H23C	0.5472	0.6933	0.8441	0.134*
C24	0.40327 (10)	0.70542 (8)	0.71426 (14)	0.0559 (4)
C25	0.40935 (12)	0.77638 (10)	0.74391 (17)	0.0764 (6)
H25A	0.4365	0.7888	0.8081	0.092*
C26	0.37478 (14)	0.82749 (10)	0.6770 (2)	0.0852 (6)
H26A	0.3787	0.8745	0.6968	0.102*
C27	0.33500 (13)	0.81056 (9)	0.58258 (18)	0.0753 (5)
H27A	0.3124	0.8457	0.5382	0.090*
C28	0.32851 (10)	0.74105 (8)	0.55344 (14)	0.0571 (4)
H28A	0.3012	0.7297	0.4889	0.068*
C29	0.36178 (9)	0.68726 (7)	0.61803 (12)	0.0471 (3)
C30	0.35171 (9)	0.61351 (7)	0.58128 (11)	0.0425 (3)
C31	0.32200 (9)	0.55565 (7)	0.65384 (11)	0.0432 (3)
H31A	0.3539	0.5121	0.6385	0.052*
H31B	0.3345	0.5682	0.7264	0.052*
C32	0.21917 (9)	0.54897 (6)	0.63193 (10)	0.0392 (3)
C33	0.25150 (9)	0.49995 (7)	0.46692 (10)	0.0413 (3)
C34	0.33334 (9)	0.53628 (7)	0.44029 (11)	0.0441 (3)

C35	0.38566 (11)	0.51050 (8)	0.35770 (12)	0.0569 (4)
H35A	0.4393	0.5342	0.3390	0.068*
C36	0.35971 (12)	0.45104 (9)	0.30367 (13)	0.0637 (4)
H36A	0.3974	0.4335	0.2516	0.076*
C37	0.27742 (12)	0.41713 (8)	0.32667 (13)	0.0606 (4)
H37A	0.2588	0.3777	0.2887	0.073*
C38	0.22379 (11)	0.44208 (7)	0.40568 (12)	0.0519 (4)
H38A	0.1676	0.4201	0.4191	0.062*
C39	0.15199 (9)	0.57447 (7)	0.70743 (11)	0.0422 (3)
C40	0.05604 (10)	0.56137 (8)	0.69350 (12)	0.0494 (3)
C41	−0.00595 (11)	0.58597 (10)	0.76695 (14)	0.0652 (4)
H41A	−0.0689	0.5761	0.7585	0.078*
C42	0.02448 (13)	0.62447 (10)	0.85140 (14)	0.0698 (5)
H42A	−0.0180	0.6414	0.8990	0.084*
C43	0.11783 (13)	0.63835 (9)	0.86631 (14)	0.0663 (4)
H43A	0.1384	0.6645	0.9239	0.080*
C44	0.18026 (11)	0.61337 (8)	0.79572 (12)	0.0538 (4)
H44A	0.2432	0.6225	0.8068	0.065*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0438 (5)	0.0878 (8)	0.0628 (7)	0.0181 (5)	0.0026 (5)	0.0208 (6)
O2	0.0564 (7)	0.0758 (8)	0.0750 (8)	−0.0069 (6)	−0.0080 (6)	−0.0162 (7)
O3	0.0425 (6)	0.0874 (8)	0.0620 (7)	−0.0059 (5)	−0.0029 (5)	−0.0114 (6)
O4	0.0652 (7)	0.0771 (8)	0.0722 (8)	−0.0082 (6)	−0.0198 (6)	−0.0206 (6)
N1	0.0391 (6)	0.0400 (6)	0.0493 (7)	−0.0002 (4)	0.0022 (5)	0.0001 (5)
N2	0.0435 (6)	0.0420 (6)	0.0474 (7)	−0.0035 (5)	−0.0002 (5)	0.0011 (5)
N3	0.0473 (6)	0.0432 (6)	0.0521 (7)	−0.0064 (5)	0.0072 (5)	−0.0041 (5)
N4	0.0427 (6)	0.0381 (6)	0.0452 (6)	−0.0036 (4)	−0.0023 (5)	−0.0021 (5)
C1	0.0623 (11)	0.1324 (19)	0.0994 (16)	0.0450 (12)	0.0042 (11)	0.0306 (14)
C2	0.0424 (7)	0.0522 (8)	0.0437 (8)	0.0031 (6)	0.0032 (6)	−0.0023 (6)
C3	0.0435 (8)	0.0716 (10)	0.0607 (10)	0.0048 (7)	0.0122 (7)	−0.0038 (8)
C4	0.0651 (10)	0.0660 (10)	0.0547 (9)	−0.0082 (8)	0.0222 (8)	−0.0035 (8)
C5	0.0714 (10)	0.0551 (9)	0.0472 (9)	−0.0060 (7)	0.0047 (8)	0.0063 (7)
C6	0.0480 (7)	0.0443 (7)	0.0506 (8)	−0.0019 (6)	−0.0031 (6)	0.0007 (6)
C7	0.0396 (6)	0.0369 (6)	0.0429 (7)	−0.0017 (5)	0.0002 (5)	−0.0038 (6)
C8	0.0354 (6)	0.0390 (6)	0.0441 (7)	0.0000 (5)	−0.0037 (5)	0.0008 (6)
C9	0.0417 (7)	0.0383 (7)	0.0497 (8)	0.0034 (5)	−0.0006 (6)	0.0040 (6)
C10	0.0467 (7)	0.0314 (6)	0.0469 (8)	−0.0015 (5)	0.0003 (6)	0.0063 (6)
C11	0.0370 (6)	0.0454 (7)	0.0432 (7)	0.0030 (5)	−0.0022 (6)	0.0035 (6)
C12	0.0362 (6)	0.0434 (7)	0.0432 (7)	0.0042 (5)	−0.0006 (5)	0.0010 (6)
C13	0.0413 (7)	0.0551 (8)	0.0557 (9)	0.0036 (6)	−0.0019 (6)	−0.0099 (7)
C14	0.0463 (8)	0.0774 (11)	0.0497 (9)	0.0111 (7)	0.0002 (7)	−0.0134 (8)
C15	0.0419 (8)	0.0804 (11)	0.0503 (9)	0.0075 (7)	0.0088 (7)	0.0053 (8)
C16	0.0377 (7)	0.0576 (9)	0.0556 (9)	−0.0012 (6)	0.0024 (6)	0.0067 (7)
C17	0.0566 (8)	0.0346 (7)	0.0475 (8)	0.0002 (6)	0.0013 (6)	0.0043 (6)
C18	0.0629 (9)	0.0440 (8)	0.0557 (9)	−0.0010 (7)	−0.0057 (8)	−0.0008 (7)

C19	0.0870 (13)	0.0557 (10)	0.0631 (11)	−0.0022 (9)	−0.0127 (10)	−0.0091 (8)
C20	0.1116 (16)	0.0561 (10)	0.0551 (10)	0.0029 (10)	0.0012 (11)	−0.0098 (8)
C21	0.0915 (13)	0.0573 (10)	0.0635 (11)	0.0058 (9)	0.0200 (10)	−0.0020 (8)
C22	0.0659 (10)	0.0474 (8)	0.0605 (10)	0.0000 (7)	0.0090 (8)	−0.0006 (7)
C23	0.0719 (12)	0.1237 (18)	0.0724 (13)	0.0040 (11)	−0.0153 (10)	−0.0411 (13)
C24	0.0391 (7)	0.0593 (9)	0.0694 (10)	−0.0088 (6)	0.0057 (7)	−0.0184 (8)
C25	0.0629 (10)	0.0737 (12)	0.0928 (14)	−0.0171 (9)	0.0091 (10)	−0.0399 (11)
C26	0.0800 (13)	0.0479 (10)	0.1281 (19)	−0.0087 (9)	0.0134 (13)	−0.0257 (12)
C27	0.0713 (11)	0.0462 (9)	0.1090 (16)	−0.0036 (8)	0.0178 (11)	−0.0067 (10)
C28	0.0502 (8)	0.0459 (8)	0.0757 (11)	−0.0070 (6)	0.0134 (8)	−0.0019 (8)
C29	0.0354 (6)	0.0460 (7)	0.0604 (9)	−0.0094 (5)	0.0117 (6)	−0.0106 (7)
C30	0.0338 (6)	0.0433 (7)	0.0505 (8)	−0.0050 (5)	0.0030 (6)	−0.0057 (6)
C31	0.0431 (7)	0.0414 (7)	0.0450 (8)	−0.0022 (5)	−0.0051 (6)	−0.0006 (6)
C32	0.0432 (7)	0.0312 (6)	0.0429 (7)	−0.0039 (5)	−0.0019 (6)	0.0035 (5)
C33	0.0445 (7)	0.0372 (6)	0.0418 (7)	0.0027 (5)	−0.0055 (6)	−0.0009 (6)
C34	0.0486 (7)	0.0407 (7)	0.0428 (7)	0.0013 (6)	−0.0004 (6)	−0.0021 (6)
C35	0.0570 (9)	0.0615 (9)	0.0523 (9)	0.0014 (7)	0.0078 (7)	−0.0054 (8)
C36	0.0746 (11)	0.0649 (10)	0.0517 (9)	0.0137 (8)	0.0055 (8)	−0.0133 (8)
C37	0.0765 (11)	0.0498 (9)	0.0551 (10)	0.0038 (8)	−0.0088 (8)	−0.0147 (7)
C38	0.0569 (8)	0.0454 (8)	0.0529 (9)	−0.0017 (6)	−0.0088 (7)	−0.0060 (7)
C39	0.0472 (7)	0.0376 (7)	0.0416 (7)	−0.0015 (5)	0.0015 (6)	0.0058 (6)
C40	0.0463 (8)	0.0545 (8)	0.0473 (8)	0.0024 (6)	−0.0006 (6)	0.0076 (7)
C41	0.0482 (8)	0.0863 (12)	0.0614 (11)	0.0079 (8)	0.0052 (8)	0.0049 (9)
C42	0.0720 (11)	0.0819 (12)	0.0561 (10)	0.0181 (9)	0.0151 (9)	0.0007 (9)
C43	0.0770 (12)	0.0682 (10)	0.0539 (10)	0.0026 (9)	0.0079 (8)	−0.0107 (8)
C44	0.0574 (9)	0.0540 (9)	0.0503 (9)	−0.0043 (7)	0.0037 (7)	−0.0048 (7)

Geometric parameters (Å, °)

C1—O1	1.4135 (19)	C23—H23A	0.9600
C1—H1A	0.9600	C23—H23B	0.9600
C1—H1B	0.9600	C23—H23C	0.9600
C1—H1C	0.9600	C24—O4	1.363 (2)
C2—O1	1.3670 (17)	C24—C29	1.397 (2)
C2—C3	1.386 (2)	C24—C25	1.404 (2)
C2—C7	1.3993 (18)	C25—C26	1.380 (3)
C3—C4	1.375 (2)	C25—H25A	0.9300
C3—H3A	0.9300	C26—C27	1.361 (3)
C4—C5	1.373 (2)	C26—H26A	0.9300
C4—H4A	0.9300	C27—C28	1.376 (2)
C5—C6	1.380 (2)	C27—H27A	0.9300
C5—H5A	0.9300	C28—C29	1.392 (2)
C6—C7	1.3873 (19)	C28—H28A	0.9300
C6—H6A	0.9300	C29—C30	1.4852 (18)
C7—C8	1.4831 (18)	C30—N3	1.2863 (17)
C8—N1	1.2859 (16)	C30—C31	1.5068 (19)
C8—C9	1.5114 (18)	C31—C32	1.5057 (18)
C9—C10	1.5030 (18)	C31—H31A	0.9700
C9—H9A	0.9700	C31—H31B	0.9700

C9—H9B	0.9700	C32—N4	1.2989 (16)
C10—N2	1.2961 (17)	C32—C39	1.4636 (19)
C10—C17	1.470 (2)	C33—N4	1.4015 (17)
C11—C16	1.3978 (19)	C33—C38	1.4028 (19)
C11—N2	1.4061 (17)	C33—C34	1.4140 (19)
C11—C12	1.4144 (18)	C34—C35	1.398 (2)
C12—C13	1.4019 (19)	C34—N3	1.4082 (17)
C12—N1	1.4077 (17)	C35—C36	1.372 (2)
C13—C14	1.371 (2)	C35—H35A	0.9300
C13—H13A	0.9300	C36—C37	1.386 (2)
C14—C15	1.389 (2)	C36—H36A	0.9300
C14—H14A	0.9300	C37—C38	1.369 (2)
C15—C16	1.367 (2)	C37—H37A	0.9300
C15—H15A	0.9300	C38—H38A	0.9300
C16—H16A	0.9300	C39—C44	1.401 (2)
C17—C22	1.399 (2)	C39—C40	1.4108 (19)
C17—C18	1.412 (2)	C40—O3	1.3524 (18)
C18—O2	1.349 (2)	C40—C41	1.390 (2)
C18—C19	1.393 (2)	C41—C42	1.367 (3)
C19—C20	1.368 (3)	C41—H41A	0.9300
C19—H19A	0.9300	C42—C43	1.379 (3)
C20—C21	1.380 (3)	C42—H42A	0.9300
C20—H20A	0.9300	C43—C44	1.372 (2)
C21—C22	1.379 (2)	C43—H43A	0.9300
C21—H21A	0.9300	C44—H44A	0.9300
C22—H22A	0.9300	O2—H2	0.95 (2)
C23—O4	1.423 (2)	O3—H3	0.97 (2)
O1—C1—H1A	109.5	H23A—C23—H23C	109.5
O1—C1—H1B	109.5	H23B—C23—H23C	109.5
H1A—C1—H1B	109.5	O4—C24—C29	116.23 (13)
O1—C1—H1C	109.5	O4—C24—C25	123.90 (16)
H1A—C1—H1C	109.5	C29—C24—C25	119.84 (17)
H1B—C1—H1C	109.5	C26—C25—C24	119.43 (18)
O1—C2—C3	124.15 (13)	C26—C25—H25A	120.3
O1—C2—C7	115.80 (12)	C24—C25—H25A	120.3
C3—C2—C7	119.97 (14)	C27—C26—C25	121.33 (17)
C4—C3—C2	119.87 (14)	C27—C26—H26A	119.3
C4—C3—H3A	120.1	C25—C26—H26A	119.3
C2—C3—H3A	120.1	C26—C27—C28	119.42 (19)
C5—C4—C3	121.16 (15)	C26—C27—H27A	120.3
C5—C4—H4A	119.4	C28—C27—H27A	120.3
C3—C4—H4A	119.4	C27—C28—C29	121.72 (17)
C4—C5—C6	119.02 (15)	C27—C28—H28A	119.1
C4—C5—H5A	120.5	C29—C28—H28A	119.1
C6—C5—H5A	120.5	C28—C29—C24	118.25 (14)
C5—C6—C7	121.43 (14)	C28—C29—C30	118.52 (13)
C5—C6—H6A	119.3	C24—C29—C30	123.23 (14)
C7—C6—H6A	119.3	N3—C30—C29	117.51 (13)
C6—C7—C2	118.53 (13)	N3—C30—C31	120.58 (12)

C6—C7—C8	120.45 (12)	C29—C30—C31	121.52 (12)
C2—C7—C8	121.00 (12)	C32—C31—C30	103.84 (10)
N1—C8—C7	118.45 (11)	C32—C31—H31A	111.0
N1—C8—C9	121.56 (12)	C30—C31—H31A	111.0
C7—C8—C9	119.90 (11)	C32—C31—H31B	111.0
C10—C9—C8	105.37 (10)	C30—C31—H31B	111.0
C10—C9—H9A	110.7	H31A—C31—H31B	109.0
C8—C9—H9A	110.7	N4—C32—C39	119.75 (11)
C10—C9—H9B	110.7	N4—C32—C31	119.50 (12)
C8—C9—H9B	110.7	C39—C32—C31	120.75 (12)
H9A—C9—H9B	108.8	N4—C33—C38	116.16 (12)
N2—C10—C17	118.76 (12)	N4—C33—C34	125.03 (12)
N2—C10—C9	119.36 (12)	C38—C33—C34	118.52 (13)
C17—C10—C9	121.87 (12)	C35—C34—N3	117.05 (13)
C16—C11—N2	117.27 (12)	C35—C34—C33	118.42 (13)
C16—C11—C12	118.85 (13)	N3—C34—C33	124.03 (12)
N2—C11—C12	123.59 (12)	C36—C35—C34	121.53 (15)
C13—C12—N1	115.82 (12)	C36—C35—H35A	119.2
C13—C12—C11	118.28 (13)	C34—C35—H35A	119.2
N1—C12—C11	125.80 (12)	C35—C36—C37	120.09 (15)
C14—C13—C12	121.55 (14)	C35—C36—H36A	120.0
C14—C13—H13A	119.2	C37—C36—H36A	120.0
C12—C13—H13A	119.2	C38—C37—C36	119.59 (14)
C13—C14—C15	119.61 (14)	C38—C37—H37A	120.2
C13—C14—H14A	120.2	C36—C37—H37A	120.2
C15—C14—H14A	120.2	C37—C38—C33	121.64 (15)
C16—C15—C14	120.16 (14)	C37—C38—H38A	119.2
C16—C15—H15A	119.9	C33—C38—H38A	119.2
C14—C15—H15A	119.9	C44—C39—C40	117.41 (13)
C15—C16—C11	121.30 (14)	C44—C39—C32	121.37 (12)
C15—C16—H16A	119.4	C40—C39—C32	121.22 (12)
C11—C16—H16A	119.4	O3—C40—C41	117.84 (14)
C22—C17—C18	117.63 (14)	O3—C40—C39	122.34 (13)
C22—C17—C10	121.25 (13)	C41—C40—C39	119.82 (14)
C18—C17—C10	121.08 (13)	C42—C41—C40	120.87 (16)
O2—C18—C19	117.61 (15)	C42—C41—H41A	119.6
O2—C18—C17	122.49 (14)	C40—C41—H41A	119.6
C19—C18—C17	119.90 (16)	C41—C42—C43	120.35 (16)
C20—C19—C18	120.56 (17)	C41—C42—H42A	119.8
C20—C19—H19A	119.7	C43—C42—H42A	119.8
C18—C19—H19A	119.7	C44—C43—C42	119.61 (16)
C19—C20—C21	120.72 (17)	C44—C43—H43A	120.2
C19—C20—H20A	119.6	C42—C43—H43A	120.2
C21—C20—H20A	119.6	C43—C44—C39	121.92 (15)
C22—C21—C20	119.43 (18)	C43—C44—H44A	119.0
C22—C21—H21A	120.3	C39—C44—H44A	119.0
C20—C21—H21A	120.3	C8—N1—C12	120.24 (11)
C21—C22—C17	121.74 (16)	C10—N2—C11	121.26 (11)
C21—C22—H22A	119.1	C30—N3—C34	119.96 (12)

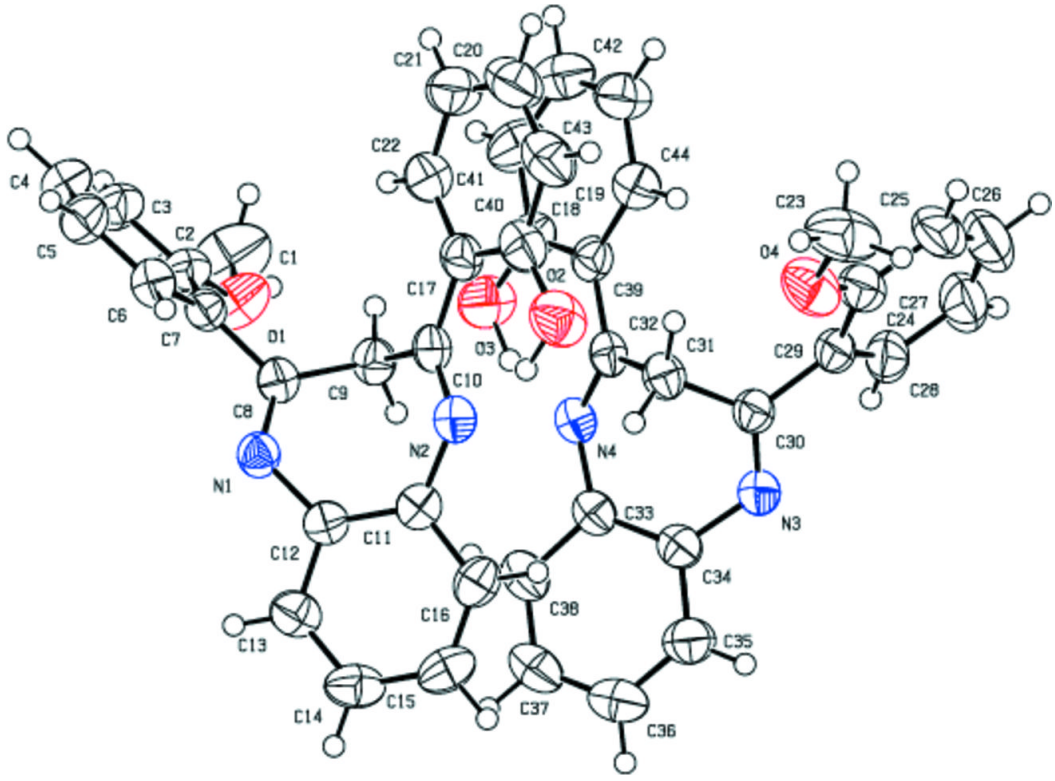
C17—C22—H22A	119.1	C32—N4—C33	121.76 (11)
O4—C23—H23A	109.5	C2—O1—C1	119.08 (13)
O4—C23—H23B	109.5	C18—O2—H2	102.9 (13)
H23A—C23—H23B	109.5	C40—O3—H3	105.1 (12)
O4—C23—H23C	109.5	C24—O4—C23	118.95 (15)
O1—C2—C3—C4	177.88 (14)	C25—C24—C29—C30	−179.36 (14)
C7—C2—C3—C4	1.2 (2)	C28—C29—C30—N3	35.31 (18)
C2—C3—C4—C5	−0.4 (2)	C24—C29—C30—N3	−144.51 (14)
C3—C4—C5—C6	−0.8 (2)	C28—C29—C30—C31	−137.55 (13)
C4—C5—C6—C7	1.1 (2)	C24—C29—C30—C31	42.63 (19)
C5—C6—C7—C2	−0.4 (2)	N3—C30—C31—C32	−75.57 (15)
C5—C6—C7—C8	−178.67 (13)	C29—C30—C31—C32	97.07 (14)
O1—C2—C7—C6	−177.77 (12)	C30—C31—C32—N4	72.36 (14)
C3—C2—C7—C6	−0.8 (2)	C30—C31—C32—C39	−106.82 (13)
O1—C2—C7—C8	0.54 (19)	N4—C33—C34—C35	−177.08 (13)
C3—C2—C7—C8	177.48 (13)	C38—C33—C34—C35	−3.49 (19)
C6—C7—C8—N1	47.73 (17)	N4—C33—C34—N3	−5.4 (2)
C2—C7—C8—N1	−130.55 (14)	C38—C33—C34—N3	168.15 (13)
C6—C7—C8—C9	−128.98 (13)	N3—C34—C35—C36	−172.87 (14)
C2—C7—C8—C9	52.74 (17)	C33—C34—C35—C36	−0.7 (2)
N1—C8—C9—C10	−68.35 (16)	C34—C35—C36—C37	3.5 (2)
C7—C8—C9—C10	108.26 (13)	C35—C36—C37—C38	−2.0 (2)
C8—C9—C10—N2	74.87 (15)	C36—C37—C38—C33	−2.3 (2)
C8—C9—C10—C17	−103.74 (13)	N4—C33—C38—C37	179.17 (13)
C16—C11—C12—C13	1.80 (18)	C34—C33—C38—C37	5.0 (2)
N2—C11—C12—C13	−171.80 (12)	N4—C32—C39—C44	−171.24 (12)
C16—C11—C12—N1	177.98 (12)	C31—C32—C39—C44	7.94 (19)
N2—C11—C12—N1	4.4 (2)	N4—C32—C39—C40	8.15 (19)
N1—C12—C13—C14	178.51 (13)	C31—C32—C39—C40	−172.67 (12)
C11—C12—C13—C14	−4.9 (2)	C44—C39—C40—O3	178.72 (13)
C12—C13—C14—C15	3.6 (2)	C32—C39—C40—O3	−0.7 (2)
C13—C14—C15—C16	1.0 (2)	C44—C39—C40—C41	−1.0 (2)
C14—C15—C16—C11	−4.2 (2)	C32—C39—C40—C41	179.63 (13)
N2—C11—C16—C15	176.69 (13)	O3—C40—C41—C42	−177.90 (15)
C12—C11—C16—C15	2.7 (2)	C39—C40—C41—C42	1.8 (2)
N2—C10—C17—C22	−170.77 (13)	C40—C41—C42—C43	−1.4 (3)
C9—C10—C17—C22	7.85 (19)	C41—C42—C43—C44	0.1 (3)
N2—C10—C17—C18	7.11 (19)	C42—C43—C44—C39	0.7 (3)
C9—C10—C17—C18	−174.27 (12)	C40—C39—C44—C43	−0.3 (2)
C22—C17—C18—O2	179.03 (14)	C32—C39—C44—C43	179.13 (14)
C10—C17—C18—O2	1.1 (2)	C7—C8—N1—C12	−178.55 (11)
C22—C17—C18—C19	−1.0 (2)	C9—C8—N1—C12	−1.89 (18)
C10—C17—C18—C19	−178.93 (14)	C13—C12—N1—C8	−143.21 (13)
O2—C18—C19—C20	−178.76 (16)	C11—C12—N1—C8	40.53 (19)
C17—C18—C19—C20	1.3 (2)	C17—C10—N2—C11	171.77 (11)
C18—C19—C20—C21	−0.7 (3)	C9—C10—N2—C11	−6.89 (18)
C19—C20—C21—C22	−0.2 (3)	C16—C11—N2—C10	144.76 (13)
C20—C21—C22—C17	0.4 (3)	C12—C11—N2—C10	−41.54 (18)
C18—C17—C22—C21	0.2 (2)	C29—C30—N3—C34	−167.67 (11)

C10—C17—C22—C21	178.10 (14)	C31—C30—N3—C34	5.27 (19)
O4—C24—C25—C26	177.51 (16)	C35—C34—N3—C30	−145.17 (14)
C29—C24—C25—C26	−0.5 (2)	C33—C34—N3—C30	43.09 (19)
C24—C25—C26—C27	−0.2 (3)	C39—C32—N4—C33	175.85 (11)
C25—C26—C27—C28	0.5 (3)	C31—C32—N4—C33	−3.34 (18)
C26—C27—C28—C29	−0.1 (3)	C38—C33—N4—C32	148.59 (12)
C27—C28—C29—C24	−0.5 (2)	C34—C33—N4—C32	−37.68 (19)
C27—C28—C29—C30	179.65 (14)	C3—C2—O1—C1	10.8 (2)
O4—C24—C29—C28	−177.34 (13)	C7—C2—O1—C1	−172.45 (16)
C25—C24—C29—C28	0.8 (2)	C29—C24—O4—C23	170.62 (14)
O4—C24—C29—C30	2.5 (2)	C25—C24—O4—C23	−7.5 (2)

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O2—H2···N2	0.95 (2)	1.69 (2)	2.5749 (18)	154 (2)
O3—H3···N4	0.97 (2)	1.71 (2)	2.5921 (16)	150.6 (18)
C9—H9B···O1	0.97	2.42	2.8971 (17)	110
C31—H31B···O4	0.97	2.25	2.8830 (18)	122

Fig. 1


C21
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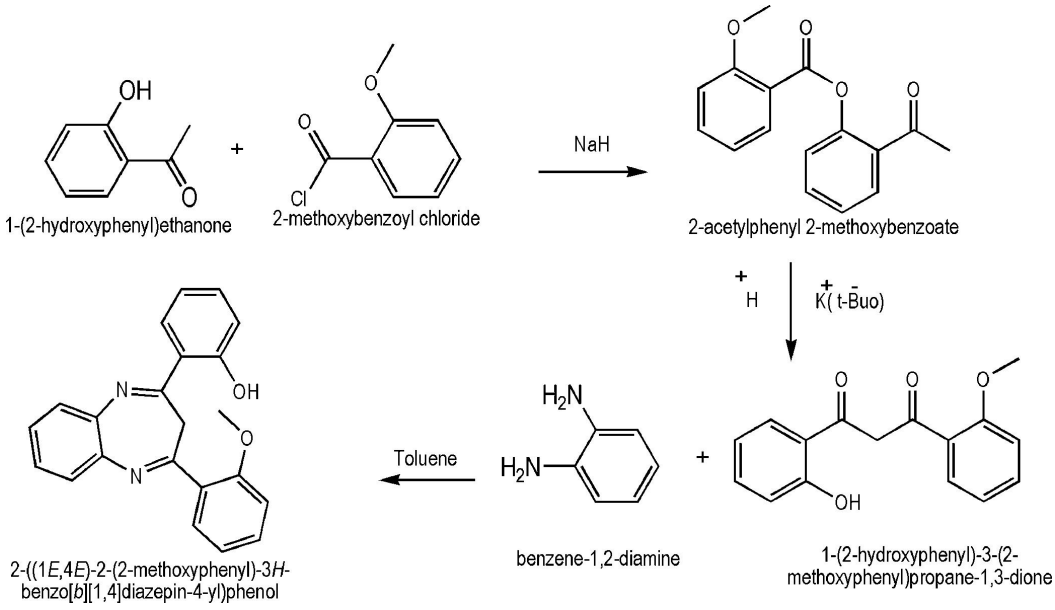
C36

Fig. 2


OH
O
1-(2-hydroxyphenyl)ethanone
+
O
O
Cl
2-methoxybenzoyl chloride
NaH
O
O
O
O
2-acetylphenyl 2-methoxybenzoate
+
H
+
K(t-Buo)
O
O
O
OH
1-(2-hydroxyphenyl)-3-(2-methoxyphenyl)propane-1,3-dione
+
H2N
H2N
benzene-1,2-diamine
Toluene
N
N
OH
O
2-((1E,4E)-2-(2-methoxyphenyl)-3H-benzo[b][1,4]diazepin-4-yl)phenol