Crystal structure of 2,3-dihydro-2,2-di(pyridin-2-yl)-1*H*-benzo[*d*]-imidazole, $C_{17}H_{14}N_4$

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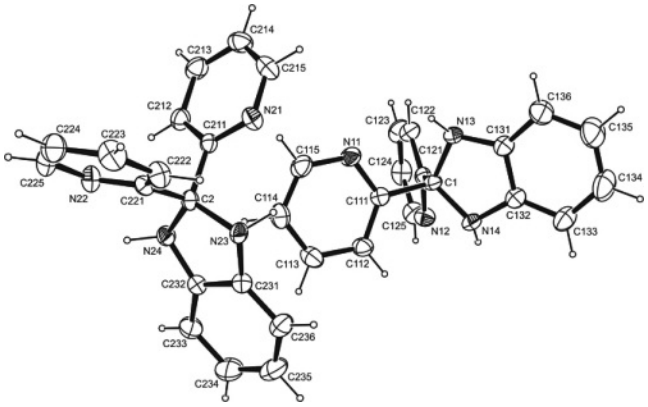

Abstract

$C_{17}H_{14}N_4$, orthorhombic, $P2_12_12_1$ (no. 19), a = 10.3837(3) Å, b = 10.4793(3) Å, c = 26.7515(7) Å, V = 2910.9 Å^3, Z = 8, $R_{gt}(F)$ = 0.0341, $wR_{ref}(F^2)$ = 0.0909, T = 200 K.

Table 1. Data collection and handling.

Crystal:	green blocks, size 0.246×0.423×0.563 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	0.78 cm^{-1}
Diffractometer, scan mode:	Bruker APEX-II CCD, φ and ω
$2\theta_{max}$:	56.62°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	28411, 4063
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 3748
$N(param)_{refined}$:	396
Programs:	SHELX, WinGX, MERCURY, PLATON [7–10]

Source of material

The compound was obtained upon reacting ortho-phenylendiamin and 2,2'-diazabenzophenone with $Re_2(CO)_4Br_2$ in toluene. Crystals suitable for the diffraction study were obtained upon free evaporation of the solvent at ambient conditions.

Experimental details

Carbon-bound H atoms were placed in calculated positions (C–H 0.95 Å) and were included in the refinement in the riding model approximation, with U_{iso}(H) set to 1.2U_{eq}(C). All nitrogen-bound H atoms were located on a difference Fourier map and refined freely. Due to the absence of a strong anomalous scatterer, the Flack parameter is meaningless. Thus, Friedel opposites (3169 pairs) have been merged and the item was removed from the CIF.

Discussion

Next to cardiovascular diseases, cancer has become one of the main fatal diseases in industrialized countries. Apart from classical surgery, chemo- and radiotherapeutic treatments have entered the arsenal of possible cures for certain types of cancer. All methods, however, suffer from their own set of problematic side-effects and, as a consequence, the development of radiopharmaceuticals – combining the advantages of chemotherapy as well as radiation methods while at the same time avoiding their unique respective undesired side-effects – has been a topic of research [1, 2]. Tailoring and fine-tuning of the envisioned radiopharmaceuticals' properties such as lipophilicity and, in particular, inertness is of paramount importance with respect to possible future *in vivo* applications in contemporary medicine and requires sound knowledge about structural parameters of the ligands applied if a more heuristic approach in the synthesis is to triumph over pure trial-and-error as it is encountered in this specific field of coordination chemistry up to the present day. In addition, the spatial requirements of pharmaceuticals are of importance as this factor influences on their interaction with enzymatic systems and, as a consequence, the pathway and rate of conjugation, functionalization and secretion from the body. In continuation of our ongoing research on the field of rhenium coordination compounds [1, 2], the double Schiff-base derived from semicarbazide and dipyridylketone was reacted with $Re_2(CO)_4Br_2$. A structural analysis of the crystalline reaction product showed the formation of an unexpected compound. The title compound is a derivative of benzimidazole and crystallizes with two complete molecules in the asymmetric unit. The carbon atom of the five-membered sub ring is bonded to two pyridyl moieties in their respective *ortho* positions with regards to the nitrogen atoms. A conformational analysis of the two five-membered rings according to Cremer & Pople [3] is precluded by the low puckering amplitudes (τ = 3.0° and τ = 4.9°, respectively). The nitrogen atoms of the pyridyl groups point in two different directions within each of the two complete molecules present in the asymmetric unit. The least-squares planes as defined by the non-hydrogen atoms of the respective aromatic systems enclose angles of 42.17(6)°, 54.39(5)° and 83.63(4)° within the first molecule and 46.48(6)°, 62.33(6)° and 83.78(4)° within the second molecule. In the crystal, classical hydrogen bonds of the N–H···N type are observed next to C–H···N contacts whose range falls below the sum of van-der-Waals radii of the atoms participating in them [4]. The hydrogen bonds exclusively apply NH groups as donors and nitrogen atoms as acceptors in between one of the specific molecules and its symmetry-generated equivalents. No contacts of the mentioned kind exist in between the two different molecules present in the asymmetric unit. The two different molecules are, therefore, connected to individual chains along the crystallographic *a* axis in the one case and along the crystallographic *b* axis in the other case. In terms of graph-set analysis [5, 6], the descriptor for these contacts is $C^1_1(5)C^1_1(5)C^1_1(5)C^1_1(5)$ on the unary level. The C–H···N contacts exist between one of the hydrogen atoms on a pyridyl moiety

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as the donor and the nitrogen atom of one of the two NH groups as acceptor in each of the two molecules. The descriptor for these contacts would be $C^1_1(5)C^1_1(5)$ on the unary level. In addition, a series of C–H···π contacts is apparent that exclusively appear in between the two molecules present in the asymmetric unit. This latter kind of contact is mutually established by hydrogen atoms on the pyridyl moieties in each case and applies two aromatic systems as as well as the center of gravity constituted by the five-membered rings in each case as acceptors. The shortest intercentroid distance between two centers of gravity was measured at 3.7650(10) Å and is observed in between one pyridine ring and a phenyl group of one of the two molecules present in the asymmetric unit and its symmetry-generated equivalent.

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

Atom	Site	*x*	*y*	*z*	U_{iso}
H(112)	4*a*	0.3988	0.6458	0.1910	0.034
H(113)	4*a*	0.2485	0.6148	0.1261	0.041
H(114)	4*a*	0.1854	0.4051	0.1059	0.042
H(115)	4*a*	0.2762	0.2363	0.1491	0.042
H(122)	4*a*	0.3997	0.2943	0.3157	0.037
H(123)	4*a*	0.2479	0.3277	0.3798	0.047
H(124)	4*a*	0.1771	0.5369	0.3962	0.047
H(125)	4*a*	0.2603	0.7035	0.3494	0.044
H(133)	4*a*	0.8366	0.6916	0.2573	0.046
H(134)	4*a*	1.0291	0.5762	0.2697	0.063
H(135)	4*a*	1.0264	0.3552	0.2744	0.064
H(136)	4*a*	0.8314	0.2422	0.2681	0.049
H(212)	4*a*	0.0831	0.1358	0.0571	0.032
H(213)	4*a*	0.1144	–0.0262	0.1171	0.040
H(214)	4*a*	0.3253	–0.0932	0.1354	0.041
H(215)	4*a*	0.4964	0.0027	0.0942	0.039
H(222)	4*a*	0.4416	0.1655	–0.0664	0.036
H(223)	4*a*	0.4103	0.0290	–0.1351	0.045
H(224)	4*a*	0.2004	–0.0389	–0.1545	0.045
H(225)	4*a*	0.0295	0.0359	–0.1069	0.043
H(233)	4*a*	0.0345	0.5788	0.0151	0.045
H(234)	4*a*	0.1504	0.7720	0.0204	0.061
H(235)	4*a*	0.3737	0.7729	0.0174	0.061
H(236)	4*a*	0.4892	0.5812	0.0066	0.046
H(13)	4*a*	0.577(2)	0.292(2)	0.2347(8)	0.038(6)
H(14)	4*a*	0.571(2)	0.650(2)	0.2678(7)	0.037(6)
H(23)	4*a*	0.440(2)	0.321(2)	0.0204(7)	0.031(5)
H(24)	4*a*	0.081(2)	0.324(2)	–0.0161(7)	0.029(5)

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

Atom	Site	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
N(11)	4*a*	0.3846(2)	0.3369(1)	0.19529(5)	0.0397(8)	0.0225(6)	0.0251(6)	–0.0037(6)	–0.0045(6)	–0.0024(5)
N(12)	4*a*	0.3757(1)	0.6023(1)	0.30607(5)	0.0344(7)	0.0263(6)	0.0257(6)	0.0039(6)	0.0017(6)	–0.0033(5)
N(13)	4*a*	0.5920(1)	0.3564(1)	0.25746(5)	0.0269(6)	0.0171(6)	0.0288(6)	0.0011(5)	–0.0016(6)	–0.0020(5)
N(14)	4*a*	0.5958(1)	0.5787(1)	0.24831(5)	0.0286(7)	0.0172(6)	0.0278(6)	–0.0036(5)	0.0004(6)	–0.0008(5)
N(21)	4*a*	0.3952(1)	0.1213(1)	0.05211(5)	0.0225(6)	0.0328(7)	0.0245(6)	0.0025(6)	–0.0009(5)	0.0027(5)
N(22)	4*a*	0.1306(1)	0.1398(1)	–0.05908(5)	0.0244(6)	0.0375(8)	0.0243(6)	–0.0036(6)	–0.0028(5)	–0.0042(6)
N(23)	4*a*	0.3747(1)	0.3433(1)	–0.00201(5)	0.0155(5)	0.0242(6)	0.0295(6)	–0.0028(5)	–0.0009(5)	0.0001(5)
N(24)	4*a*	0.1500(1)	0.3410(1)	0.00627(5)	0.0171(6)	0.0237(6)	0.0281(6)	0.0019(5)	–0.0014(5)	–0.0009(5)
C(1)	4*a*	0.5076(2)	0.4686(1)	0.25239(5)	0.0276(7)	0.0155(6)	0.0223(6)	–0.0008(6)	0.0003(5)	–0.0001(6)
C(2)	4*a*	0.2626(1)	0.2568(1)	–0.00042(6)	0.0142(6)	0.0236(6)	0.0226(6)	–0.0006(5)	0.0003(5)	–0.0003(5)
C(111)	4*a*	0.4191(2)	0.4562(2)	0.20685(5)	0.0258(7)	0.0229(7)	0.0190(6)	0.0004(6)	0.0019(6)	–0.0023(6)
C(112)	4*a*	0.3715(2)	0.5624(2)	0.18203(6)	0.0357(8)	0.0226(7)	0.0279(8)	0.0018(7)	–0.0019(7)	–0.0016(6)
C(113)	4*a*	0.2831(2)	0.5440(2)	0.14372(6)	0.040(1)	0.0341(9)	0.0291(8)	0.0083(8)	–0.0052(7)	0.0019(7)
C(114)	4*a*	0.2464(2)	0.4206(2)	0.13165(6)	0.0368(9)	0.043(1)	0.0245(8)	–0.0014(8)	–0.0067(7)	–0.0038(7)
C(115)	4*a*	0.3002(2)	0.3208(2)	0.15795(6)	0.046(1)	0.0313(9)	0.0274(8)	–0.0088(8)	–0.0048(8)	–0.0037(7)
C(121)	4*a*	0.4157(1)	0.4827(2)	0.29706(5)	0.0241(7)	0.0237(7)	0.0194(6)	–0.0021(6)	–0.0032(6)	–0.0011(6)
C(122)	4*a*	0.3701(2)	0.3778(2)	0.32335(6)	0.0361(9)	0.0268(8)	0.0294(8)	–0.0052(7)	0.0016(7)	–0.0005(6)
C(123)	4*a*	0.2803(2)	0.3976(2)	0.36096(7)	0.041(1)	0.044(1)	0.0319(9)	–0.0132(9)	0.0053(8)	0.0039(8)
C(124)	4*a*	0.2388(2)	0.5206(2)	0.37070(7)	0.0336(9)	0.056(1)	0.0275(8)	–0.0031(9)	0.0057(7)	–0.0076(8)
C(125)	4*a*	0.2889(2)	0.6192(2)	0.34254(7)	0.0401(9)	0.0380(9)	0.0314(8)	0.0068(8)	0.0028(8)	–0.0078(7)
C(131)	4*a*	0.7202(2)	0.4006(2)	0.25966(6)	0.0277(8)	0.0255(7)	0.0255(7)	0.0000(6)	0.0023(6)	–0.0041(6)
C(132)	4*a*	0.7213(2)	0.5339(2)	0.25683(6)	0.0287(8)	0.0261(7)	0.0246(7)	–0.0013(6)	0.0022(6)	–0.0031(6)
C(133)	4*a*	0.8355(2)	0.6012(2)	0.25988(8)	0.0327(9)	0.0357(9)	0.047(1)	–0.0083(8)	0.0058(8)	–0.0034(8)
C(134)	4*a*	0.9495(2)	0.5320(2)	0.2669(1)	0.0283(9)	0.057(1)	0.072(2)	–0.0078(9)	0.006(1)	–0.010(1)
C(135)	4*a*	0.9479(2)	0.4003(2)	0.2698(1)	0.029(1)	0.054(1)	0.077(2)	0.0084(9)	0.001(1)	–0.011(1)
C(136)	4*a*	0.8325(2)	0.3327(2)	0.26615(8)	0.0327(9)	0.0359(9)	0.054(1)	0.0082(8)	0.0015(9)	–0.0068(9)
C(211)	4*a*	0.2749(1)	0.1587(1)	0.04203(5)	0.0206(6)	0.0211(6)	0.0187(6)	–0.0011(6)	–0.0021(5)	–0.0028(5)
C(212)	4*a*	0.1672(2)	0.1068(2)	0.06522(6)	0.0236(7)	0.0295(8)	0.0276(7)	–0.0039(7)	0.0000(6)	0.0005(6)
C(213)	4*a*	0.1860(2)	0.0115(2)	0.10055(6)	0.0374(9)	0.0323(9)	0.0301(8)	–0.0100(7)	0.0018(7)	0.0041(7)
C(214)	4*a*	0.3100(2)	–0.0281(2)	0.11143(6)	0.046(1)	0.0299(8)	0.0265(8)	0.0013(8)	–0.0028(7)	0.0061(7)
C(215)	4*a*	0.4113(2)	0.0295(2)	0.08658(6)	0.0313(8)	0.0370(9)	0.0300(8)	0.0079(8)	–0.0055(7)	0.0031(7)
C(221)	4*a*	0.2503(1)	0.1766(1)	–0.04826(5)	0.0232(7)	0.0238(7)	0.0185(6)	0.0010(6)	–0.0012(6)	0.0021(5)
C(222)	4*a*	0.3577(2)	0.1375(2)	–0.07537(6)	0.0251(8)	0.0370(9)	0.0277(8)	0.0032(7)	0.0008(6)	–0.0025(7)
C(223)	4*a*	0.3391(2)	0.0569(2)	–0.11570(6)	0.039(1)	0.044(1)	0.0297(8)	0.0094(8)	0.0031(7)	–0.0086(8)
C(224)	4*a*	0.2155(2)	0.0174(2)	–0.12733(6)	0.050(1)	0.0377(9)	0.0241(7)	–0.0009(9)	–0.0049(8)	–0.0077(7)
C(225)	4*a*	0.1144(2)	0.0618(2)	–0.09845(6)	0.0352(9)	0.044(1)	0.0290(8)	–0.0077(8)	–0.0063(7)	–0.0068(7)
C(231)	4*a*	0.3292(2)	0.4686(2)	0.00491(6)	0.0250(7)	0.0246(7)	0.0259(7)	–0.0011(6)	–0.0016(6)	0.0016(6)
C(232)	4*a*	0.1948(2)	0.4676(2)	0.00731(6)	0.0246(7)	0.0245(7)	0.0251(7)	–0.0003(6)	–0.0041(6)	0.0019(6)
C(233)	4*a*	0.1259(2)	0.5794(2)	0.01331(8)	0.0350(9)	0.0277(8)	0.051(1)	0.0079(7)	–0.0093(8)	–0.0007(8)
C(234)	4*a*	0.1954(2)	0.6937(2)	0.0167(1)	0.051(1)	0.0244(9)	0.077(2)	0.0085(8)	–0.011(1)	0.0002(9)
C(235)	4*a*	0.3286(2)	0.6943(2)	0.0146(1)	0.052(1)	0.0245(9)	0.076(2)	–0.0083(9)	–0.008(1)	0.003(1)
C(236)	4*a*	0.3978(2)	0.5809(2)	0.00836(8)	0.0330(9)	0.0307(9)	0.051(1)	–0.0073(8)	–0.0035(8)	0.0037(8)

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