The crystal structure of (1R, 2R)-N₁,N₂-diferrocenyl-1,2-cyclohexanedicarboxamide, C₂₈H₃₀Fe₂N₂O₂

Abstract
C₂₈H₃₀Fe₂N₂O₂, monoclinic, P2₁ (no. 4), a = 10.7490(10) Å, b = 9.8370(8) Å, c = 11.9621(13) Å, β = 113.030(4)°, V = 1164.04(19) Å³, Z = 2, R(F) = 0.0358, wR2(F²) = 0.0612, Flack parameter = −0.007(11), T = 150(2) K.

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The 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.

Table 1: Data collection and handling.

| Crystal: | Bar, orange |
| Size: | 0.27 × 0.07 × 0.07 mm |
| Wavelength: | Mo Kα radiation (0.71073 Å) |
| μ: | 1.28 mm⁻¹ |
| Diffractometer, scan mode: | Bruker APEX-II, φ and ω-scans |
| θmax, completeness: | 28°, >99% |
| N(hkl)measured, N(hkl)unique, Rint: | 13446, 5616, 0.038 |
| Criterion for Iobs, N(hkl)gt: | Iobs > 2σ(Iobs), 4852 |
| N(param)refined: | 307 |
| Programs: | SHELX [2, 3], PLATON [4], Bruker programs [5, 6], |

Source of material
Ferrocenecarboxylic acid (244 mg, 1.1 mmol) and 1-hydroxybenzotriazole (205 mg, 1.5 mmol) were dissolved in anhydrous dichloromethane (20 mL) by gentle heating in a reaction flask equipped with a stirring bar under an argon atmosphere. The solution was cooled on ice and neat 1-ethyl-3-[3-(dimethylamino)propyl]carbodiimide (0.26 mL, 1.5 mmol) was introduced, causing the partly precipitated acid to redissolve. After stirring the mixture at 0 °C for 15 min, a dichloromethane solution of (1R, 2R)-1,2-diaminocyclohexane (60 mg, 0.50 mmol in 10 mL) was added and the stirring was continued at 0 °C 5 min and then at room
temperature overnight. Then, the reaction mixture was washed with saturated aqueous NaHCO3 and brine (twice each), dried over anhydrous MgSO4, and evaporated under reduced pressure. The residue was purified by column chromatography over silica gel using dichloromethane-methanol (20:1) as the eluent. The first minor band containing \([\text{[IH-benzotriazol-1-ylxoy]carbonyl]ferrocene [1]}\) (63 mg, 17\%) was followed by a major orange band due to the product. Following evaporation, the title compound was isolated as an orange amorphous solid (216 mg, 76\%). Single crystals were grown by slow cooling of a methanolic solution.

1H NMR (CDCl3, 399.95 MHz): δ = 1.41 (m, 4 H), 1.83 (m, 2 H) and 2.25 (m, 2 H) (4 × CH of C6H10), 3.84 (m, 2 H, 2 CH of C6H10), 4.09 (s, 10 H, C5H5), 4.30 (m, 4 H, 4 × CH of C6H10), 171.31 (s, 2 C, C=O of C5H4), 130.2 (s), 127.3 (m), 124.7 (w), 122.1 (w), 118.4 (m), 114.0 (v), 32.2 (w), 31.2 (w), 30.8 (m), 162.5 (s, ν(C=O)), 1545 (s, 4 × CH of C5H5), 1411 (m), 1353 (m), 1344 (m), 1320 (m), 1273 (m), 1247 (w), 1221 (w), 1184 (m), 1140 (w), 1085 (v), 1048 (w), 1022 (m), 1015 (m), 1003 (m), 955 (v), 928 (w), 888 (w), 865 (w), 821 (m), 812 (m), 773 (m), 762 (w), 648 (br w), 608 (w), 584 (w), 530 (w), 519 (m), 504 (m), 497 (m), 484 (m), 462 (m), 445 (w), 430 (w) cm\(^{-1}\). MS (ESI+); m/z = 561.1 ([M + Na\(^{+}\)]). Anal. Calc. for C26H10Fe2N2O2 (538.24 g mol\(^{-1}\)): C 62.48, H 5.62, N 5.21\%. Found: C 62.15, H 5.68, N 5.04\%.

Experimental details

The structure was solved by Direct methods using SHELX-97 [2] and then refined by least-squares routine based on \(F^2\) (SHELXL-2017 [3]). Hydrogen atoms attached to nitrogen atoms were identified on the difference electron density maps and refined as riding atoms with \(U_{iso}(H) = 1.2 \times U_{eq}(N)\) [3]. All other hydrogen atoms were included in their calculated
positions with $U_{eq}(H) = 1.2 \ U_{eq}(C)$. The structural drawing and all numerical parameters discussed below were obtained with a recent version of the PLATON program [4]. The absolute configuration determined by anomalous dispersion [7] corresponded to that declared for the starting diamine (cf. Table 1).

Discussion

Carboxamides obtained from chiral diamines and phosphinocarboxylic acids emerged as efficient auxiliary ligands for a range enantioselective transition-metal catalyzed reactions [8]. In the chemistry of ferrocene-based ligands, compounds of this type are represented by amides obtained from 1,2-diaminocyclohexanes and planar-chiral 2-(diphenylphosphino)ferrocene-1-carboxylic acid [8–10]. Because none of these compound appears to have been structurally characterized, we decided to synthesize and characterize an analogous compound without the phosphine substituents at the ferrocene moieties, viz. (IR, 2R)-N1,N2-diferrocenyl-1,2-cyclohexanedicarboxamide. This compound was prepared by amidation of (IR, 2R)-diaminocyclohexane with ferrocenecarboxylic acid in the presence of peptide coupling agents [11] and was isolated as an orange solid in 76% yield by column chromatography. Chromatographic purification also afforded some [(H-benztotriazol-1-yloxy)carbonyl]ferrocene, representing a non-consumed reaction intermediate.

The compound crystallizes in the non-centrosymmetric space group $P2_1_2$ and two molecules in the unit cell. The central six-membered ring in each dinuclear title complex has a chair conformation, which is manifested by the ring puckering coordinate $\theta$ [12] being 176.7(4)$^\circ$ (Note: ideal chair has a chair conformation, which is manifested by the ring central six-membered ring in each dinuclear title complex corresponds to that declared for the starting diamine (cf. Table 1). The pivotal C—N bonds occupy equatorial positions and their length (C1—N1 = 1.465(2) Å, C2—N2 = 1.462(5) Å) as well as the N1—C21—C2—N2 torsion angle of $–56.2(4)^\circ$ are similar to those in the parent amine, (IR, 2R)-diaminocyclohexane [1.465(2) Å and $–59.2(1)^\circ$, respectively] [13].

The ferrocene moieties in the title compound adopt the usual geometry with the individual Fe—C distances falling into narrow ranges, 2.025(4) Å (C11) to 2.056(3) Å (C13), and 2.026(3) Å (C31) to 2.053(5) Å (C33) for the ferrocene units comprising Fe1 and Fe2, respectively. Correspondingly, the dihedral angles subtended by the least-squares planes of the cyclopentadienyl rings are only 3.2(3)$^\circ$ (Fe1) and 3.7(3)$^\circ$ (Fe2). Even so, the amide substituents are rotated only slightly from the planes of their bonding cyclopentadienyl rings. In this case, however, a smaller departure from a coplanar arrangement is observed for the ferrocene unit comprising atom Fe1 that for the other ferrocene moiety (compare the angle between the C(21, N1, O1) and C(11–15) planes of 4.2(4)$^\circ$ with that subtended by the planes {C41, N2, O2} and C(31–35) of 76(4)$^\circ$). The amide planes are oriented so that their NH groups point to the same face of the cyclohexane ring. The dihedral angle subtended by the amide planes {C21, N1, O1} and {C41, N2, O2} is 79.6(5)$^\circ$.

Adjacent molecules related by the crystallographic 2 screw axes are interconnected via pairs of N—H···O hydrogen bonds into infinite columnar stacks oriented in the direction of the crystallographic $b$ axis (see Figure) [14]. These interactions are supported by the relatively weaker C—H···O interactions between the ferrocene CH groups adjacent to the amide NH (C15 and C35) as the donors and the amide C=O moieties as the acceptors. The hydrogen bond parameters are as follows: N1—H1N···O2$^i$: N1···O2 = 3.008(4) Å, angle at H1N = 155$^\circ$; N2—H2N···O1$^i$: N2···O1 = 2.947(4) Å, angle at H2N = 154$^\circ$; C15—H15···O2$^i$: C15···O2 = 3.325(5) Å, angle at H15 = 158$^\circ$; and C35—H35···O1$^i$: C35···O1 = 3.304(5) Å, angle at H35 = 138$^\circ$; where $i = 1 – x, –1/2 + y, 1 – z$.

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References