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THE CRYSTAL AND MOLECULAR STRUCTURE OF TETRABENZO-[b,f,h,l]-1,4,11-OXADIAZACYCLOTRIDECAN-5,10-DIONE***

$C_{29}H_{29}N_3O_4$, M = 479,50, monoclinic, P 2$_1$/n, a = 9,286(2), b = 13,854(3), c = 19,588(3) A, β = 86.25(2)°, V = 2514.5(9) A^3, Z = 4, D_x = 1.2665(5) g · cm^{-3}, λ(CuK_α) = 1.54178 A, μ = 0.66 mm^{-1}, F(000) = 1008, diffractometer measurement at room temp., R = 4.4% for 2572 observed reflections with I > 3σ (I). Hydrogen bonds of type N-H...O = C between the molecule of compound and one molecule of solvent with N...O distance of 2.901 A.

INTRODUCTION

The title compound was obtained by G l i n k a [1] from the reaction of aminoaryl ether and diphenyl acid dichloride in a two--phases solvent: water-benzene. The confirmation of the formula of the compound was done by elemental, IR, ^{1}HNMR and MS analysis. The ability of the compound to complexing of sodium, iron and copper ions might be utilized in pharmaceutical industry.

EXPERIMENTAL

Colouress crystals were obtained from benzene : DMF : ethanol (2 : 1 : 1) solution, room temp., average crystal size ab. 0.6 mm, mp. 275-277 K. Cell parameters and intensity data measured on Enraf

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Table 1

Final positional and thermal parameters ($*10^4$) with e.s. d.'s in parentheses

$U_{iso} = 1/3\ \Sigma_i\ \Sigma_j U_{ij} a_i^* a_j^* a_i a_j$

Atoms	X	Y	Z	$U_{iso}(A^2)$
1	2	3	4	5
O1	1 901(2)	8 676(1)	1 771(1)	583(6)
C1	1 198(3)	7 939(2)	1 402(1)	573(10)
C2	733(4)	8 125(3)	735(2)	831(13)
C3	-6(4)	7 433(3)	355(2)	982(17)
C4	-255(4)	6 551(3)	641(2)	951(16)
C5	175(4)	6 375(3)	1 316(2)	756(13)
C6	894(3)	7 071(2)	1 708(1)	532(9)
N1	1 275(2)	6 896(2)	2 411(1)	499(7)
C7	435(3)	7 218(2)	2 905(1)	474(9)
O2	-584(2)	7 754(1)	2 770(1)	689(8)
C8	798(2)	6 848(2)	3 610(1)	477(8)
C9	1 231(3)	5 900(2)	3 703(2)	620(11)
C10	1 452(4)	5 507(3)	4 344(2)	817(14)
C11	1 254(4)	6 063(3)	4 905(2)	885(16)
C12	827(4)	6 998(3)	4 826(2)	744(13)
C13	582(3)	7 416(2)	4 189(1)	525(9)
C14	66(3)	8 435(2)	4 159(1)	549(9)
C15	-1 289(3)	8 641(2)	4 391(2)	728(11)
C16	-1 814(4)	9 565(3)	4 376(2)	890(14)
C17	-1 001(5)	10 305(3)	4 137(2)	915(15)
C18	353(4)	10 117(2)	3 913(2)	749(12)
C19	894(3)	9 190(2)	3 933(1)	554(9)
C20	2 369(3)	8 975(2)	3 706(1)	582(10)
O3	3 271(3)	8 546(2)	4 060(1)	1 175(11)
N2	2 569(2)	9 181(2)	3 055(1)	555(7)
C21	3 678(3)	8 805(2)	2 679(1)	509(9)
C22	5 091(3)	8 710(2)	2 936(2)	652(11)
C23	6 099(3)	8 297(2)	2 539(2)	815(13)
C24	5 711(4)	7 988(2)	1 896(2)	889(15)
C25	4 318(3)	8 088(2)	1 624(2)	718(12)
C26	3 310(3)	8 502(2)	2 019(1)	509(8)
C1R	6 613(5)	5 104(4)	2 926(3)	1 602(28)
C2R	6 866(5)	6 272(4)	3 842(2)	1 271(20)
N1R	5 984(3)	5 832(2)	3 304(1)	723(10)
C3R	4 665(3)	6 131(2)	3 135(2)	667(11)
O4R	3 872(2)	5 829(1)	2 669(1)	691(7)
H2	917(34)	8 741(24)	552(16)	
H3	-323(38)	7 528(26)	-127(20)	
H4	-751(35)	6 072(24)	355(16)	
H5	-1(29)	5 816(21)	1 542(14)	
HN1	1 987(27)	6 582(18)	2 545(12)	
H9	1 279(27)	5 497(19)	3 303(13)	
H10	1 744(36)	4 833(25)	4 406(17)	
H11	1 465(35)	5 832(24)	5 335(17)	

Table 1 (contd)

1	2	3	4	5
H12	765(30)	7 345(20)	5 204(14)	
H15	-1 877(26)	8 117(18)	4 550(12)	
H16	-2 794(35)	9 658(23)	4 557(16)	
H17	-1 444(30)	10 950(20)	4 099(14)	
H18	991(26)	10 606(18)	3 810(12)	
HN2	1 856(22)	9 372(16)	2 816(10)	
H22	5 290(24)	8 869(17)	3 393(11)	
H23	7 078(27)	8 233(19)	2 750(12)	
H24	6 289(31)	7 656(21)	1 640(14)	
H25	3 999(31)	7 874(21)	1 162(14)	
H1R1	7 658(5)	4 903(4)	3 092(3)	
H1R2	6 749(5)	5 616(4)	2 511(3)	
H1R3	6 066(5)	4 470(4)	2 754(3)	
H2R1	6 250(5)	6 865(4)	4 070(2)	
H2R2	7 921(5)	6 527(4)	3 660(2)	
H2R3	6 978(5)	5 714(4)	4 219(2)	
HOR4	4 430(38)	6 684(27)	3 509(18)	

Table 2

Interatomic distances (A)

O1-C1	1.4328(31)	C14-C19	1.3552(38)
O1-C26	1.4454(33)	C15-C16	1.3708(50)
C1-C2	1.4260(45)	C16-C17	1.3394(58)
C1-C6	1.3649(37)	C17-C18	1.3301(58)
C2-C3	1.4180(57)	C18-C19	1.3805(40)
C3-C4	1.3577(58)	C19-C20	1.4432(38)
C4-C5	1.4269(56)	C20-O3	1.2695(37)
C5-C6	1.4255(48)	C20-N2	1.3080(28)
C6-N1	1.4641(29)	N2-C21	1.3323(32)
N1-C7	1.2826(30)	C21-C22	1.4418(41)
C7-O2	1.2448(33)	C21-C26	1.4220(30)
C7-C8	1.5310(30)	C22-C23	1.3088(44)
C8-C9	1.3890(39)	C23-C24	1.3995(54)
C8-C13	1.3841(32)	C24-C25	1.4375(49)
C9-C10	1.3959(55)	C25-C26	1.3073(40)
C10-C11	1.3447(56)	C1R-N1R	1.3601(60)
C11-C12	1.3664(58)	C2R-N1R	1.5052(52)
C12-C13	1.4075(45)	N1R-C3R	1.3544(40)
C13-C14	1.4932(39)	C3R-O4R	1.2800(40)
C14-C15	1.3403(39)	C3R-HOR4	1.0725(362)

Table 3

Bond angles (°)

C1	O1	C26	120.2(2)	C16	C17	C18	117.7(4)
O1	C1	C6	119.6(2)	C17	C18	C19	120.7(3)
O1	C1	C2	120.6(3)	C14	C19	C18	121.8(3)
C2	C1	C6	119.7(3)	C18	C19	C20	121.5(3)
C1	C2	C3	123.0(3)	C14	C19	C20	116.6(3)
C2	C3	C4	117.9(4)	C19	C20	N2	109.1(2)
C3	C4	C5	119.1(4)	C19	C20	O3	125.1(2)
C4	C5	C6	123.6(3)	O3	C20	N2	125.3(3)
C1	C6	C5	116.7(2)	C20	N2	C21	120.6(2)
C5	C6	N1	123.0(3)	N2	C21	C26	113.3(2)
C1	C6	N1	120.2(2)	N2	C21	C22	122.1(2)
C6	N1	C7	118.7(2)	C22	C21	C26	124.7(3)
N1	C7	C8	113.9(2)	C21	C22	C23	117.7(3)
N1	C7	O2	118.7(2)	C22	C23	C24	116.9(3)
O2	C7	C8	127.3(2)	C23	C24	C25	126.5(3)
C7	C8	C13	121.3(2)	C24	C25	C26	116.7(3)
C7	C8	C9	121.2(2)	C21	C26	C25	117.5(2)
C9	C8	C13	117.2(2)	O1	C26	C25	120.2(2)
C8	C9	C10	123.2(3)	O1	C26	C21	122.2(2)
C9	C10	C11	119.4(4)	C1R	N1R	C2R	116.6(3)
C10	C11	C12	118.4(4)	C2R	N1R	C3R	126.1(3)
C11	C12	C13	123.7(3)	C1R	N1R	C3R	117.2(3)
C8	C13	C12	118.0(3)	N1R	C3R	HOR4	101.4(1.9)
C12	C13	C14	119.7(2)	N1R	C3R	O4R	130.2(3)
C8	C13	C14	122.3(2)	O4R	C3R	HOR4	128.3(1.9)
C13	C14	C19	124.5(3)	C6	N1	HN1	128.1(1.6)
C13	C14	C15	119.0(3)	C7	N1	HN1	113.2(1.6)
C15	C14	C19	116.5(3)	C20	N2	HN2	121.5(1.3)
C14	C15	C16	121.3(3)	C21	N2	HN2	114.0(1.3)
C15	C16	C17	121.9(4)				

Table 4

Selected torsion angles (°)

Atoms				Angle	Atoms				Angle
C1	C6	N1	C7	87.0(3)	C20	N2	C21	C26	138.6(3)
C1	C6	N1	HN1	-101.4(2.1)	HN2	N2	C21	C26	-19.4(1.5)
HN1	N1	C7	C8	-7.8(1.8)	C19	C20	N2	HN2	-4.5(1.6)
C6	N1	C7	O2	-7.7(4)	O3	C20	N2	C21	11.3(4)
HN1	N1	C7	O2	174.4(1.8)	O3	C20	N2	HN2	167.6(1.6)

Table 5

Puckering parameters [5]

Q2 = 1.7609(26)	
Q3 = 0.4932(25)	
Q4 = 1.0698(29)	
Q5 = 0.4523(28)	
Q6 = 0.4872(28)	
PHI 2 = 62.88(8)	
PHI 3 = -7.03(32)	
PHI 4 = 72.95(13)	
PHI 5 = -75.13(33)	
PHI 6 = -82.99(30)	
Total puckering amplitude QT = 2.2205(28)	
Spherical polar angles:	
THETA 2 = 74.35(8)	
THETA 3 = 24.75(12)	
THETA 4 = 67.08(14)	
THETA 5 = 42.87(24)	

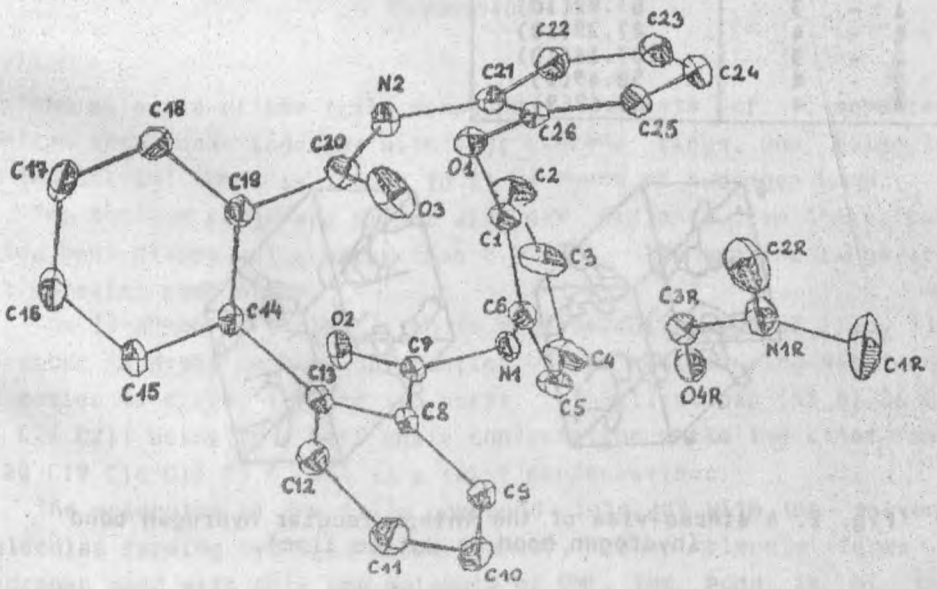

Fig. 1. The molecular structure with the atom numbering scheme

Table 6

Calculeted best planes

Plane 1		Plane 2	
	D(A)		D(A)
M1 = 0.854(1)	C1 0.0146(27)	M1 = 0.953(1)	C8 0.0013(20)
M2 = -0.343(1)	C2 -0.0076(38)	M2 = 0.287(1)	C9 0.0005(28)
M3 = -0.400(1)	C3 -0.0167(38)	M3 = -0.098(1)	C10 -0.0047(38)
D = -3.756(13)	C4 0.0187(38)	D = 3.183(15)	C11 0.0029(38)
	C5 0.0031(38)		C12 0.0028(38)
	C6 -0.0134(27)		C13 -0.0036(28)
Plane 3		**Plane 4**	
	D(A)		D(A)
M1 = -0.358(1)	C14 0.0092(21)	M1 = 0.240(1)	C21 -0.0086(27)
M2 = -0.153(1)	C15 -0.0124(38)	M2 = 0.893(1)	C22 0.0054(30)
M3 = -0.921(1)	C16 -0.0062(39)	M3 = -0.381(1)	C23 0.0030(30)
D = -9.498(15)	C17 0.0078(40)	D = 9.805(9)	C24 -0.0065(30)
	C18 0.0112(39)		C25 0.0009(30)
	C19 -0.0089(21)		C26 0.0061(27)

Dihedral angles (°)	
Plane-Plane	Angles(°)
1 - 2	41.11(10)
1 - 3	83.92(10)
1 - 4	87.29(10)
2 - 3	107.16(10)
2 - 4	58.49(9)
3 - 4	82.62(9)

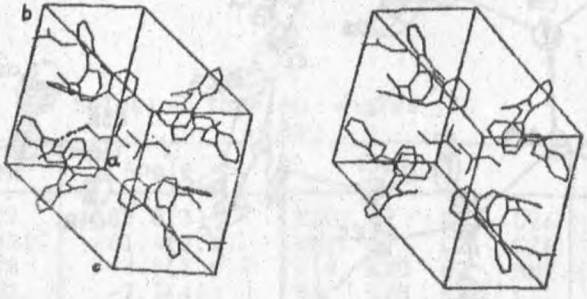

Fig. 2. A stereo-view of the intermolecular hydrogen bond (hydrogen bond as dotted line)

Nonius CAD-4 diffractometer. Lattice parameters determined by least-squares refinement using 15 reflections. 2612 independent

reflections measured to a θ_{max} 66.85°, range of h k l:0 to 10, 0 to 15, -21 to 21 respectively, data not corrected for absorption. 2572 reflections with $I > 3\sigma(I)$ considered as observed and used in subsequent calculations. Structure solved by direct methods using SHELX86 [2]; first E-map revealed positions of all non-H atoms; least squares refinement using SHELX76 [3], isotropic and then anisotropic temperature factors, H atoms located on difference Fourier map and included in the refinement with isotropic temperature factors; refinement to the ultimate value of R = 4.4%. In the last cycle, max shift/e.s.d. was 0.110 for all refined parameters. Lowest peaks on final difference Fourier map were 0.146 and -0.245 eA^{-3}. Scattering factors from CRYSRULER [4]. Atomic coordinates are given in Tab. 1, interatomic distances in Tab. 2, angles in Tab. 3. Selected dihedral angles are given in Tab. 4, the puckering parameters [5] in Tab. 5 and calculated best planes in Tab. 6.

The molecular structure with the atom numbering scheme is shown in Fig. 1. A stereo-view of the intermolecular hydrogen bond is shown in Fig. 2.

DISCUSSION

The molecule of the title compound consists of 13-membered central ring fused together with four benzene rings. One molecule of the solvent (DMF) is linked to it by means of hydrogen bond.

The benzene rings are planar with max. distance from the calculated best planes not greater than 0.0187 A. The benzene rings are not parallel each other.

The 13-membered central ring is considerably puckered (Tab. 5). In order to describe the conformation of the central ring was found it easier to divide it into two parts. The first par (N2 N1 C6 C1 O1 C26 C21) being in a half chair conformation while the other one (C20 C19 C14 C13 C8 C7 N1) in a twist conformation.

The molecules of the title compound interact with the solvent molecules forming hydrogen bonds. Namely, one molecule forms a hydrogen bond with only one molecule of DMF. The bond is of the type N-H...O where N1-HN1...O4R atoms take part with N1-O4R distance of 2.9010 A, HN1-O4R distance of 2.0656 A and N1-HN1-O4R angle

of 168.59°. It is worth while to mention, it appeared, the linkage with the second molecule of DMF (utilization of N2 atom) was impossible because of special conditions in the unit cell.

The hydrogen bond caused significant changes in torsion angles (see Tab. 4).

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STRUKTURA CZĄSTECZKI I KRYSZTAŁÓW
TETRABENZO-[b,f,h,l]-1,4,11-OXADIAZACYCLOTRIDECAN-5,10-DIONU

$C_{29}H_{29}N_3O_4$, M = 479,5, układ jednoskośny, P $2_1/n$, a = 9.286(2), b = 13.854(3), c = 19.588(3) A, β = 86,25(2)°, V = 2514.5(9) A^3, Z = 4, D_x = 1.2665(5) g · cm^{-3}, λ (CuK_α) = 1.54178 A, μ = 0.66 mm_α^{-1}, F(000) = 1008, pomiar dyfraktometryczny w temp. pokojowej, R = 4.4% dla 2572 refleksów z kryterium obserwowalności $I > 3\sigma(I)$. Wiązanie wodorowe typu N-H...O-C pomiędzy cząsteczką związku i cząsteczką rozpuszczalnika, odległość wynosi 2.901 A.