Crystal structure of 2-[3,5-bis(4-octyloxyphenyl)pyrazol-1-yl]pyridine, $C_{36}H_{47}N_3O_2$

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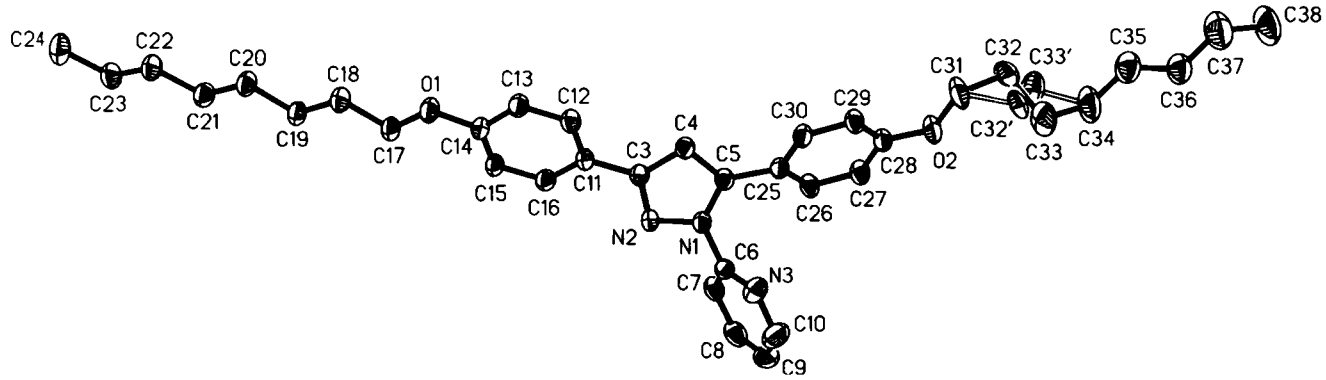
Received October 28, 2005, accepted and available on-line December 15, 2005; CCDC no. 1267/1677



Abstract

$C_{36}H_{47}N_3O_2$, monoclinic, $P12_1/c1$ (no. 14), $a = 10.751(1)$ Å, $b = 7.954(1)$ Å, $c = 38.144(5)$ Å, $\beta = 92.326(3)°$, $V = 3259.2$ Å^3, $Z = 4$, $R_{gt}(F) = 0.064$, $wR_{ref}(F^2) = 0.199$, $T = 296$ K.

Source of material

The compound was prepared as previously described [1]. Suitable crystals for X-ray diffraction were obtained from ethanol. Elemental analysis: found – C, 77.8 %; H, 8.2 %; N, 7.8 %; calc. for $C_{36}H_{47}N_3O_2$ – C, 78.1 %; H, 8.6 %; N, 7.6 %. IR and ^{1}H NMR data are available in the CIF.

Experimental details

The low N_{gt}/N_{param} ratio is due to the needle shape of the crystal and thus to the big amount of weak X-ray diffraction peaks.

Discussion

Previous works in our lab have been driven to the design, characterization and thermal study of metallomesogens built by coordination of metal fragments to mesogenic 3,5-bis(4-alkyloxyphenyl)-pyrazole ligands [2-4]. The related bi-dentate *N,N'*-donor 2-[3,5-bis(4-alkyloxyphenyl)-pyrazol-1-yl]pyridine ligands were prepared and proved to have liquid crystal properties as well as some of their complexes [1]. In this context, we think that the investigation of the molecular structure of both ligands and complexes should be of interest in order to establish potential structure/properties relationships. It is also directed to contribute to a better knowledge of the required molecular design for optimized liquid crystal properties. We describe herein the crystal structure of one of these ligands, 2-[3,5-bis(4-octyloxyphenyl)pyrazol-1-yl]pyridine.

As in other pyrazoles [2,4-6], the bond distances of the pyrazole, pyridine and benzene-substituent groups evidence a delocalized π system, which is extended to the four rings. However, the dihedral angles between the pyrazole ring and their benzene-substituents rings (23.1(1)° and 32.4(1)°) indicate the absence of planarity. The larger dihedral angle corresponds to the substituent at the 5-position, which is attributed to steric effect with the pyridine ring. As characteristic feature, the N-donor atoms (N1 and N3) present an *anti*-disposition (as reflected by the N2–N1–C6–N3 torsion angle of –118.2(4)°), possibly due to repulsion between their respective lone pairs as it has already been observed in related derivatives [5,7]. Also, in agreement with this fact, the dihedral angle between the pyrazole and pyridine rings is 57.2(2)°. However, upon complexation this ligand-type adopts a *syn*-conformation necessary for a chelation [5]. The lateral alkyl chains located in the substituents at the 3- and 5-position of the pyrazole show the characteristic single C—C distances, both chains being responsible for an elongated molecular shape. The distance between the terminal atoms of the chains (C24 and C38) of 31.44 Å is the longest one in the molecule, which then could be described as rod-like type with 31.44 Å in length towards 8.56 Å in width (measured as the distance between the C9 atom and the C24–C38 line). The molecular packing exhibits columnar and layer-like characteristics, but no short contacts are observed. In spite of the rod-like molecular shape, the studied compound did not exhibit liquid crystal behavior. This result suggests that new values of the length to width relation should be used in order to obtain mesogenic behavior. The proved liquid crystal properties of the related compounds 2-[3,5-bis(4-alkyloxyphenyl)pyrazol-1-yl]pyridine bearing longer chains (14 and 16 carbon atoms) [1] support the above suggestion.

Table 1. Data collection and handling.

Crystal:	colorless needle, size 0.05 × 0.15 × 0.50 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	0.70 cm^{-1}
Diffractometer, scan mode:	Bruker SMART CCD, φ/ω
$2\theta_{max}$:	50°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	16370, 5723
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 1881
$N(param)_{refined}$:	391
Programs:	SHELXS-97 [8], SHELXL-97 [9]

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

Atom	Site	Occ.	x	y	z	U_{iso}
H(4)	4e		0.4079	0.7904	0.2264	0.071
H(7)	4e		0.0434	1.2383	0.2538	0.084
H(8)	4e		−0.0016	1.4906	0.2824	0.111
H(9)	4e		0.1603	1.6467	0.3064	0.126
H(10)	4e		0.3546	1.5564	0.3028	0.128
H(12)	4e		0.4398	0.7741	0.1620	0.075
H(13)	4e		0.4256	0.6920	0.1042	0.076
H(15)	4e		0.1014	0.9363	0.0918	0.074
H(16)	4e		0.1171	1.0203	0.1495	0.075
H(17A)	4e		0.1440	0.9044	0.0322	0.081
H(17B)	4e		0.0787	0.7423	0.0465	0.081
H(18A)	4e		0.1878	0.5778	0.0063	0.086
H(18B)	4e		0.2464	0.7420	−0.0086	0.086
H(19A)	4e		−0.0109	0.6686	−0.0140	0.084
H(19B)	4e		0.0486	0.8316	−0.0292	0.084
H(20A)	4e		0.1012	0.5059	−0.0533	0.088
H(20B)	4e		0.1558	0.6706	−0.0690	0.088
H(21A)	4e		−0.0477	0.7483	−0.0889	0.094
H(21B)	4e		−0.0970	0.5765	−0.0751	0.094
H(22A)	4e		0.0667	0.6098	−0.1303	0.092
H(22B)	4e		0.0248	0.4358	−0.1157	0.092
H(23A)	4e		−0.1372	0.6634	−0.1501	0.102
H(23B)	4e		−0.1776	0.4875	−0.1360	0.102
H(24A)	4e		−0.0147	0.5310	−0.1908	0.162
H(24B)	4e		−0.1543	0.4761	−0.1959	0.162
H(24C)	4e		−0.0577	0.3556	−0.1770	0.162

Table 2. Continued.

Atom	Site	Occ.	x	y	z	U_{iso}
H(26)	4e		0.2311	1.0477	0.3170	0.077
H(27)	4e		0.2963	0.9858	0.3737	0.082
H(29)	4e		0.6078	0.7823	0.3390	0.077
H(30)	4e		0.5446	0.8494	0.2825	0.073
H(31A)	4e		0.6685	0.8274	0.4049	0.128
H(31B)	4e		0.6068	0.6635	0.3890	0.128
H(34A)	4e		0.5575	0.8750	0.5198	0.177
H(34B)	4e		0.5006	0.7054	0.5056	0.177
H(35A)	4e		0.6824	0.5677	0.5132	0.137
H(35B)	4e		0.7599	0.7350	0.5149	0.137
H(36A)	4e		0.6807	0.7963	0.5706	0.132
H(36B)	4e		0.6020	0.6299	0.5688	0.132
H(37A)	4e		0.8636	0.6463	0.5731	0.195
H(37B)	4e		0.7918	0.4770	0.5665	0.195
H(38A)	4e		0.7730	0.6691	0.6281	0.257
H(38B)	4e		0.8532	0.5052	0.6259	0.257
H(38C)	4e		0.7078	0.4950	0.6216	0.257
H(32A)	4e	0.5	0.5040	0.6281	0.4452	0.118
H(32B)	4e	0.5	0.6494	0.6014	0.4484	0.118
H(33A)	4e	0.5	0.5353	0.9185	0.4602	0.151
H(33B)	4e	0.5	0.6784	0.8824	0.4660	0.151
H(32C)	4e	0.5	0.7134	0.7567	0.4507	0.097
H(32D)	4e	0.5	0.6302	0.9191	0.4476	0.097
H(33C)	4e	0.5	0.5398	0.5958	0.4661	0.135
H(33D)	4e	0.5	0.4525	0.7541	0.4611	0.135

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

Atom	Site	Occ.	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
O(1)	4e		0.2610(3)	0.7498(4)	0.05820(7)	0.075(2)	0.093(2)	0.050(2)	0.012(2)	−0.009(2)	−0.013(2)
O(2)	4e		0.4868(3)	0.8464(4)	0.39651(7)	0.081(2)	0.122(3)	0.046(2)	0.024(2)	−0.006(2)	0.008(2)
N(1)	4e		0.2610(3)	1.1096(4)	0.24483(8)	0.052(2)	0.064(2)	0.049(2)	0.004(2)	−0.003(2)	−0.003(2)
N(2)	4e		0.2308(3)	1.0976(4)	0.20973(8)	0.057(2)	0.067(2)	0.041(2)	−0.000(2)	−0.007(2)	−0.000(2)
N(3)	4e		0.3224(3)	1.3470(5)	0.2766(1)	0.081(3)	0.086(3)	0.078(3)	−0.016(2)	0.006(2)	−0.016(2)
C(3)	4e		0.2913(3)	0.9611(5)	0.1992(1)	0.048(3)	0.061(3)	0.049(3)	−0.002(2)	−0.003(2)	−0.001(2)
C(4)	4e		0.3590(3)	0.8866(5)	0.2273(1)	0.055(3)	0.069(3)	0.054(3)	0.013(2)	−0.006(2)	−0.007(2)
C(5)	4e		0.3392(3)	0.9832(5)	0.2563(1)	0.049(3)	0.067(3)	0.051(3)	0.007(2)	−0.002(2)	−0.001(2)
C(6)	4e		0.2265(4)	1.2594(5)	0.2627(1)	0.058(3)	0.053(3)	0.050(3)	−0.005(2)	0.006(2)	0.003(2)
C(7)	4e		0.1064(4)	1.3046(6)	0.2639(1)	0.060(3)	0.090(4)	0.061(3)	0.017(3)	−0.003(2)	0.008(3)
C(8)	4e		0.0801(6)	1.4540(8)	0.2808(1)	0.099(4)	0.107(5)	0.072(4)	0.048(4)	0.011(3)	0.015(3)
C(9)	4e		0.1758(8)	1.5458(7)	0.2950(2)	0.162(6)	0.077(4)	0.078(4)	0.031(5)	0.023(5)	−0.004(3)
C(10)	4e		0.2908(7)	1.4913(8)	0.2927(1)	0.139(6)	0.083(5)	0.099(5)	−0.023(4)	0.009(4)	−0.021(4)
C(11)	4e		0.2812(4)	0.9090(5)	0.1624(1)	0.054(3)	0.064(3)	0.044(3)	−0.002(2)	−0.006(2)	0.000(2)
C(12)	4e		0.3718(4)	0.8084(5)	0.1480(1)	0.057(3)	0.075(3)	0.054(3)	0.002(2)	−0.006(2)	−0.001(2)
C(13)	4e		0.3634(4)	0.7581(5)	0.1133(1)	0.063(3)	0.074(3)	0.053(3)	0.013(2)	−0.004(2)	−0.008(2)
C(14)	4e		0.2614(4)	0.8070(5)	0.0923(1)	0.070(3)	0.066(3)	0.041(3)	−0.001(2)	−0.001(2)	−0.006(2)
C(15)	4e		0.1700(4)	0.9042(5)	0.1059(1)	0.070(3)	0.069(3)	0.045(3)	0.006(2)	−0.011(2)	−0.007(2)
C(16)	4e		0.1798(4)	0.9544(5)	0.1405(1)	0.063(3)	0.066(3)	0.058(3)	0.008(2)	−0.005(2)	−0.006(2)
C(17)	4e		0.1531(4)	0.7843(5)	0.0360(1)	0.074(3)	0.077(3)	0.051(3)	0.002(2)	−0.011(2)	−0.004(2)
C(18)	4e		0.1728(4)	0.6962(6)	0.0017(1)	0.075(3)	0.085(3)	0.053(3)	−0.003(3)	−0.009(2)	−0.009(2)
C(19)	4e		0.0631(4)	0.7133(5)	−0.0244(1)	0.081(3)	0.080(3)	0.049(3)	0.003(2)	−0.005(2)	−0.007(2)
C(20)	4e		0.0832(4)	0.6230(6)	−0.0584(1)	0.075(3)	0.090(3)	0.055(3)	0.006(3)	−0.010(2)	−0.013(3)
C(21)	4e		−0.0259(4)	0.6313(6)	−0.0850(1)	0.082(3)	0.088(3)	0.063(3)	0.008(3)	−0.009(3)	−0.010(3)
C(22)	4e		−0.0018(4)	0.5508(6)	−0.1199(1)	0.080(3)	0.094(4)	0.056(3)	−0.003(3)	−0.010(2)	−0.008(3)
C(23)	4e		−0.1095(4)	0.5487(6)	−0.1460(1)	0.095(4)	0.095(4)	0.062(3)	−0.002(3)	−0.016(3)	0.001(3)
C(24)	4e		−0.0815(5)	0.4708(7)	−0.1805(1)	0.128(4)	0.135(5)	0.061(3)	−0.013(4)	−0.008(3)	−0.007(3)
C(25)	4e		0.3803(4)	0.9548(5)	0.2931(1)	0.051(2)	0.062(3)	0.047(3)	0.006(2)	−0.001(2)	−0.004(2)
C(26)	4e		0.3074(4)	0.9947(5)	0.3212(1)	0.053(3)	0.086(3)	0.053(3)	0.017(2)	−0.003(2)	0.002(2)
C(27)	4e		0.3460(4)	0.9572(5)	0.3552(1)	0.064(3)	0.095(4)	0.048(3)	0.018(3)	0.007(2)	−0.002(3)
C(28)	4e		0.4592(4)	0.8767(5)	0.3620(1)	0.060(3)	0.076(3)	0.047(3)	0.009(2)	−0.005(2)	−0.001(2)
C(29)	4e		0.5320(4)	0.8365(5)	0.3347(1)	0.056(3)	0.082(3)	0.054(3)	0.012(2)	−0.008(2)	0.000(2)
C(30)	4e		0.4934(4)	0.8761(5)	0.3008(1)	0.058(3)	0.076(3)	0.049(3)	0.012(2)	−0.002(2)	−0.009(2)
C(31)	4e		0.5964(5)	0.7544(7)	0.4056(1)	0.103(4)	0.158(5)	0.057(3)	0.046(4)	−0.019(3)	0.012(3)
C(34)	4e		0.5737(6)	0.7768(8)	0.5056(1)	0.169(6)	0.211(7)	0.061(4)	0.054(6)	−0.011(4)	−0.007(4)
C(35)	4e		0.6832(5)	0.6825(7)	0.5218(1)	0.123(5)	0.142(5)	0.077(4)	0.007(4)	0.009(4)	−0.012(4)

Table 3. Continued.

Atom	Site	Occ.	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(36)	4*e*		0.6789(5)	0.6816(7)	0.5619(1)	0.120(5)	0.131(5)	0.079(4)	0.006(4)	0.001(4)	–0.001(4)
C(37)	4*e*		0.7876(6)	0.5862(9)	0.5777(1)	0.166(6)	0.215(8)	0.105(6)	0.044(6)	–0.011(5)	0.000(5)
C(38)	4*e*		0.7797(7)	0.5616(9)	0.6169(1)	0.216(7)	0.222(8)	0.075(5)	0.027(6)	–0.015(5)	0.031(5)
C(32)	4*e*	0.5	0.584(1)	0.683(1)	0.4430(2)	0.14(1)	0.08(1)	0.068(8)	0.008(8)	0.008(8)	0.029(7)
C(33)	4*e*	0.5	0.596(2)	0.834(1)	0.4673(2)	0.16(2)	0.16(2)	0.061(9)	–0.02(1)	0.019(9)	0.024(9)
C(32′)	4*e*	0.5	0.631(1)	0.798(2)	0.4444(2)	0.083(8)	0.10(1)	0.055(8)	–0.006(7)	–0.007(6)	0.040(7)
C(33′)	4*e*	0.5	0.536(1)	0.717(2)	0.4678(2)	0.10(1)	0.16(1)	0.074(9)	–0.037(9)	0.010(7)	–0.008(9)

Acknowledgments. We are grateful to the Dirección General de Investigación/ MEC of Spain (project no. BQU2003-07343) for financial support. We also thank the Comunidad de Madrid for financial support (project GR/MAT/ 0511/2004) and the contract to M.C.T.

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