Crystal structure of 2,5-dimethyl-1-(4-nitrophenyl)-1*H*-pyrrole, $C_{24}H_{24}N_4O_4$

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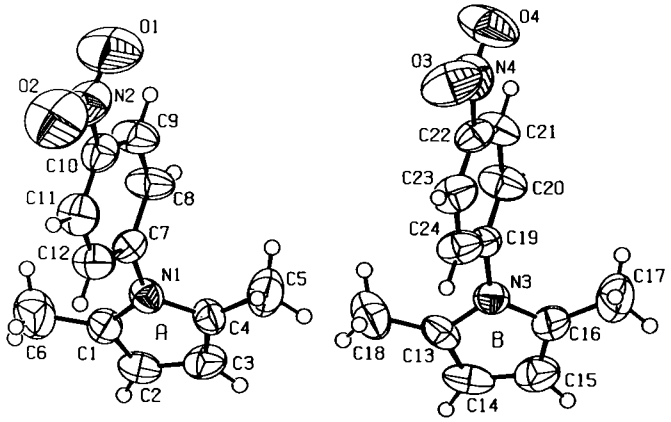

Abstract

$C_{24}H_{24}N_4O_4$, monoclinic, $P12_1/c1$ (no. 14),
$a = 12.660(6)$ Å, $b = 13.893(1)$ Å, $c = 13.448(8)$ Å,
$\beta = 104.26(5)°$, $V = 2292.4$ Å^3, $Z = 4$,
$R_{gt}(F) = 0.075$, $wR_{ref}(F^2) = 0.199$, $T = 293$ K.

Source of material

1-(*p*-nitrophenyl)-2,5-dimethyl-pyrrole was synthesized by the method of Paal-Knorr [1] in an analogous way of that described by Wolthuis [2] for 1-phenyl-2,5-dimethyl-pyrrole but using *p*-nitroaniline instead of aniline. The compound was re-crystallized several times from ethanol yielding poorly diffracting crystals.

Discussion

N-phenyl substituted pyrroles are important compounds in determining the acid/base characteristics within the pyrrole family, both at the nitrogen and at the α and β positions. Those characteristics affect the kinetic and thermodynamic parameters of the polymerization and are therefore of upmost importance in the chemical and electro-polymerization of pyrroles. The title compound was synthesized as part of our endeavor to prepare a series of phenyl substituted pyrroles for chemical polymerization.

The 2,5-dimethyl-1-(4-nitrophenyl)-pyrrole crystallizes centrosymmetrically with two independent molecules in the asymmetric unit. In each molecule the rings are mainly planar, as expected by their aromatic nature, the weighted average torsion angle of the heterocyclic ring (N1–C1–C2–C3–C4) is 0.8(3)° and of the phenyl ring (C7–C8–C9–C10–C11–C12) is 0.8(4)°; for the B molecule the values are 0.9(3)° and 1.1(4)°, respectively. The pyrrolic N—C distances are 1.375(6) Å for C1 and 1.381(7) Å for C4 and larger for C7 with 1.428(6) Å as well as in molecule B 1.384(7) Å, 1.383(6) Å and 1.431(6) Å, respectively. The NO_2 group twists very slightly out of the phenyl plane as seen by the torsion angle O2–N2–C10–C11, –2.6(9)° for molecule A and O4–N4–C22–C21, 2.0(9)° for B. The pyrrole and phenyl least-squares planes make an angle of 67.9(3)° for A and 69.0(3)° for B, much larger than the corresponding value of 15.1(2)° found for 1-(4-nitrophenyl)pyrrole [3], where the absence of the methyl substituents promotes a greater molecular planarity.

No classical hydrogen bonds are found due to the lack of conventional donors. C–H···π interactions link the molecules together in chains, exhausting the pyrrolic π system ability to act as acceptor. Molecule A directs H9 (the hydrogen atom bonded to C9) to the center of the pyrrole ring of another A molecule and directs H2 (bonded to C2) to the center of the π electron system of the pyrrole ring of a B molecule. The molecule B mimics this behavior donating H14 and H21 to the center of the pyrrole ring of A and B molecules, respectively. The structural parameters of these intermolecular interactions, the C—π distance, H···π distance and the C–H···π angle, are for H9: 3.570(6) Å, 2.648 Å, 171.4°; H2: 3.630(7) Å, 2.846 Å, 142.9°; for H14 3.529(6) Å, 2.625 Å, 164.1° and for H21 3.513(7) Å, 2.693 Å, 147.3°. Interestingly, the π electron system of the phenyl ring does not accept any proton.

Table 1. Data collection and handling.

Crystal:	yellow plate, size 0.05 × 0.24 × 0.44 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	0.87 cm^{-1}
Diffractometer, scan mode:	Enraf-Nonius Mach3, $\omega/2\theta$ (profile fit)
$2\theta_{max}$:	50.94°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	4419, 4227
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 1108
$N(param)_{refined}$:	293
Programs:	SHELXS-97 [4], SHELXL-97 [5], PLATON [6]

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

Atom	Site	*x*	*y*	*z*	U_{iso}
H(12)	4*e*	0.5574	0.3411	0.2772	0.082
H(3)	4*e*	0.2435	0.0930	0.2780	0.078
H(9)	4*e*	0.4711	0.3390	–0.0755	0.091
H(11)	4*e*	0.6750	0.4082	0.1897	0.089
H(8)	4*e*	0.3500	0.2762	0.0112	0.086
H(2)	4*e*	0.2050	0.2548	0.3417	0.072
H(5A)	4*e*	0.3775	0.1029	0.0795	0.134
H(5B)	4*e*	0.3773	0.0270	0.1657	0.134

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Table 2. Continued.

Atom	Site	x	y	z	U_{iso}
H(5C)	4e	0.4773	0.0959	0.1751	0.134
H(6A)	4e	0.2668	0.4321	0.3180	0.154
H(6B)	4e	0.3023	0.4447	0.2150	0.154
H(6C)	4e	0.3907	0.4295	0.3182	0.154
H(18A)	4e	-0.0920	0.5896	-0.0115	0.145
H(18B)	4e	-0.0462	0.5855	0.1078	0.145
H(18C)	4e	0.0336	0.5989	0.0364	0.145
H(14)	4e	-0.1608	0.7687	-0.0753	0.083

Table 2. Continued.

Atom	Site	x	y	z	U_{iso}
H(17A)	4e	0.1106	0.9418	0.2065	0.157
H(17B)	4e	0.0121	0.9374	0.2577	0.157
H(17C)	4e	0.0089	1.0082	0.1663	0.157
H(21)	4e	0.1069	0.7014	0.4639	0.080
H(24)	4e	0.1990	0.6968	0.1541	0.079
H(23)	4e	0.3197	0.6387	0.2991	0.085
H(20)	4e	-0.0143	0.7591	0.3171	0.083
H(15)	4e	-0.1262	0.9334	-0.0005	0.088

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(1)	4e	0.3712(3)	0.2589(4)	0.2079(3)	0.053(3)	0.058(4)	0.052(3)	-0.005(3)	0.018(3)	-0.007(3)
C(10)	4e	0.5828(5)	0.3789(4)	0.0495(5)	0.056(4)	0.058(4)	0.075(5)	-0.006(3)	0.030(4)	0.005(4)
C(12)	4e	0.5392(5)	0.3411(4)	0.2058(4)	0.062(4)	0.083(5)	0.057(4)	-0.018(4)	0.010(4)	0.003(4)
C(3)	4e	0.2741(4)	0.1508(5)	0.2644(4)	0.060(4)	0.075(5)	0.063(4)	-0.018(4)	0.023(3)	0.011(4)
C(9)	4e	0.4879(6)	0.3400(5)	-0.0042(5)	0.075(5)	0.105(6)	0.054(4)	-0.012(4)	0.028(4)	0.004(4)
O(1)	4e	0.6371(5)	0.4082(5)	-0.0984(5)	0.149(6)	0.190(6)	0.124(5)	-0.021(4)	0.090(5)	0.024(5)
C(11)	4e	0.6097(5)	0.3806(4)	0.1539(5)	0.060(4)	0.083(5)	0.077(5)	-0.028(4)	0.012(4)	-0.006(4)
C(8)	4e	0.4161(4)	0.3018(5)	0.0476(4)	0.054(4)	0.110(6)	0.045(4)	-0.014(4)	0.003(3)	0.011(4)
C(2)	4e	0.2523(4)	0.2422(5)	0.3002(4)	0.053(4)	0.086(5)	0.046(4)	0.001(4)	0.019(3)	0.004(4)
C(4)	4e	0.3478(4)	0.1617(5)	0.2065(4)	0.057(4)	0.052(5)	0.053(4)	-0.009(3)	0.015(3)	-0.011(4)
C(1)	4e	0.3116(5)	0.3081(5)	0.2642(4)	0.071(4)	0.055(5)	0.060(4)	0.002(4)	0.031(4)	-0.002(4)
O(2)	4e	0.7445(5)	0.4483(5)	0.0426(5)	0.103(4)	0.173(6)	0.176(7)	-0.048(4)	0.065(5)	0.006(5)
N(2)	4e	0.6604(6)	0.4150(5)	-0.0063(6)	0.090(6)	0.091(5)	0.118(7)	-0.004(4)	0.061(6)	0.017(5)
C(5)	4e	0.3995(5)	0.0907(4)	0.1519(5)	0.110(5)	0.055(5)	0.112(6)	-0.010(4)	0.047(5)	-0.008(4)
C(7)	4e	0.4424(4)	0.3017(4)	0.1530(4)	0.046(4)	0.048(4)	0.055(4)	0.000(3)	0.014(3)	0.007(3)
C(6)	4e	0.3184(5)	0.4126(5)	0.2803(5)	0.128(6)	0.088(6)	0.115(7)	-0.011(5)	0.072(5)	-0.023(5)
O(3)	4e	0.3863(4)	0.6027(4)	0.4819(4)	0.082(4)	0.134(5)	0.116(4)	0.029(3)	0.016(3)	0.049(3)
N(4)	4e	0.2991(5)	0.6325(4)	0.4886(5)	0.065(4)	0.083(5)	0.087(5)	0.016(4)	0.006(4)	-0.007(4)
C(18)	4e	-0.0374(5)	0.6142(5)	0.0455(5)	0.118(6)	0.085(6)	0.086(5)	-0.013(5)	0.022(4)	-0.031(4)
C(22)	4e	0.2230(5)	0.6661(4)	0.3934(5)	0.043(4)	0.056(4)	0.054(4)	0.008(3)	0.000(3)	0.016(3)
C(19)	4e	0.0833(5)	0.7351(4)	0.2231(4)	0.050(4)	0.046(4)	0.045(4)	0.004(3)	0.013(3)	0.004(3)
C(14)	4e	-0.1125(5)	0.7841(6)	-0.0132(4)	0.050(4)	0.118(7)	0.037(4)	0.000(4)	0.006(3)	0.010(5)
C(13)	4e	-0.0490(5)	0.7210(5)	0.0512(5)	0.061(4)	0.074(5)	0.045(4)	-0.008(4)	0.022(3)	-0.014(4)
C(17)	4e	0.0328(6)	0.9461(4)	0.1943(5)	0.145(7)	0.056(5)	0.100(6)	0.019(5)	0.003(5)	0.000(4)
C(21)	4e	0.1253(5)	0.7009(4)	0.4010(4)	0.067(5)	0.091(5)	0.042(4)	0.005(4)	0.015(4)	-0.006(4)
C(24)	4e	0.1808(5)	0.6983(4)	0.2170(4)	0.060(4)	0.083(5)	0.065(4)	0.018(4)	0.033(4)	0.019(4)
N(3)	4e	0.0100(4)	0.7737(4)	0.1335(3)	0.058(3)	0.055(4)	0.048(3)	0.003(3)	0.016(3)	0.003(3)
C(16)	4e	-0.0188(5)	0.8699(5)	0.1203(5)	0.075(5)	0.058(5)	0.055(5)	0.005(4)	0.006(4)	0.008(4)
C(23)	4e	0.2525(5)	0.6635(4)	0.3027(5)	0.064(5)	0.077(5)	0.080(5)	0.020(4)	0.030(4)	0.020(4)
C(20)	4e	0.0536(4)	0.7356(4)	0.3139(4)	0.050(4)	0.104(5)	0.050(4)	0.023(4)	0.006(3)	0.005(4)
O(4)	4e	0.2716(4)	0.6345(4)	0.5676(4)	0.126(5)	0.172(5)	0.057(3)	0.067(4)	0.001(3)	-0.001(4)
C(15)	4e	-0.0933(5)	0.8769(5)	0.0291(6)	0.076(5)	0.079(6)	0.067(5)	0.019(4)	0.021(4)	0.018(5)

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