CRYSTAL STRUCTURE OF 5-BROMO-2-(2-METHYLNITROETHENYL)FURAN

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RESUMEN. El presente trabajo describe la estructura cristalina y molecular del 5-bromo-2-(2-metilnitroetenil)furano ($C_7H_6NO_3Br$). El compuesto cristaliza en el sistema triclínico; grupo espacial P1̄; parámetros de celda: a =7 .428(2) Å, b = 10.762(3) Å, c = 10.932(4) Å, α =84 .74(3)°, β =75 .98(3)°, γ =81 .73(3)°;R = 0.065 5 para 1 587 reflexiones observadas con I >3σ(I), wR = 0.084 2. La estructura se determinó a partir de los datos de difracción de rayos X, registrados a 293(1) K y empleando los métodos directos. Los parámetros estructurales fueron refinados por mínimos cuadrados a matriz completa. Se reportan los contactos del tipo C-H···O, menores que las sumas de los radios de van der Waals, con distancias H···O < 2.7 Å . Las moléculas están empaquetadas en el cristal a través de interacciones intermoleculares débiles del tipo C-H···O y fuerzas de van der Waals.

ABSTRACT . The present paper describes the crystal and molecular structure of 5-bromo-2-(2-methylnitroethenyl)furan, ($C_7H_6NO_3Br$). The title compound crystallizes in triclinic system; space group P1̄; cell parameters: a =7 .428(2) Å, b = 10.762(3) Å, c =1 0.932(4) Å, α =84 .74(3)°, β =7 5.98(3)°, γ = 81.73(3)°; R=0 .065 5 for 1 587 observed reflections with I >3σ(I), wR =0 .084 2. The structure has been determined from X-ray diffraction data recorded at 293(1) K, and solved by direct methods. The structural parameters were refined by full-matrix least-squares analysis, to 218 refined parameters (H atoms riding). Some C-H···O intermolecular and intramolecular short contacts are noted with H···O distances < 2.7Å.T he molecules in the crystal are held together by weak intermolecular C-H···O interactions and van der Waals forces.

INTRODUCTION

As part of a continued effort in studying the structure of furanic derivatives with important bioactivities, the structure determination of a series of such compounds was carried out using x-ray diffraction.[1,2] In a previous paper the structure of 5-bromo-2-(2-nitroethenyl)furan (I), a furanic derivative with antifungal activitywas reported.[3]

From a biological point of view, the title compound (analogue of 5-bromo-2-(2-nitroethenyl)furan), has achieved prominence activity as antimycotic agents as well as a wide antifungal spectrum it is of particular clinical use in the topical treatment of superficial mycoses.4 The preparation of the title compound is reported.[5]

The x-ray structure analysis was undertaken in order to confirm the structure proposed from spectrocopy studies.

EXPERIMENTAL

The crystals of 5-bromo-2-(2-methylnitroethenyl)furan(II) have been obtained by slow evaporation from ethanol, at room temperature, controlled humidity and protected from direct light. Table I shows a summary and details of data collection, structure solution and refinement for the title compound.

Summary and details of data collection, structure solution and refinement for $C_7H_6NO_3Br$

Crystal data

$C_7H_6NO_3Br$	Dx=1 .84M gm $^{-3}$
Mr = 232.04	CuKα radiation
Triclinic	λ = 1.5418 Å
P1̄	Cell parameters from 25 reflections
a = 7.428(2) Å	θ =1 4.3- -2 8.5°
b = 10.762(3) Å	μ =6 .45m m^{-1}
c=1 0.932(4)Å	T=2 93(1)K
α = 84.74(3)°	prismatic crystal
β = 75.98(3)°	(0.17X0.20X0.35) mm
γ = 81.73(3)°	light yellow color
V = 837.6(4) Å^3	Crystal source: recrystallization from ethanol
Z=4	

Data collection

SIEMENS P3/PC diffractometer	
2θ/θ scans	$\theta_{max.}$ =5 0°
Absortion correction:	h = 7 → –6
by crystal integration	k = 10 → –10
$T_{min.}$ =0. 03	l=0 → 10

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$T_{max.}$ =0. 05

1 722 independent reflections	2 standard reflections monitored every 50 observations
1 587 observed reflections	intensity variation: less than 2 %
[I >3 σ(I)]	

Refinement

Refinement on F^2	$w=[\ \sigma^2 F+0\ .002F^2]^{-1}$
FinalR=0. 065 5	$(\Delta/\sigma)_{max.} = 0.053$
wR = 0.084 2	$\Delta\rho_{max.}$ =0. 93eÅ $^{-3}$
S=1 .24	$\Delta\rho_{min.} = -0.99\ eÅ^{-3}$
Extintion correction: not applied	
218 parameters refined	
All H-atoms riding.	

Atomic scattering factors from the International Tables for X-ray Crystallography.[6]

Computing programs used:

Computing data collection: Siemens Data Collection Software "XSCANS".[7]

Computing cell refinement:SHELXTL-Plus (PC Version).[7]

Computing data reduction:SHELXTL-Plus (PC Version).[7]

Computing structure solution:SHELXTL-Plus (PC Version). SHELXS-93.[8]

List of the structure factors, anisotropic thermal parameters, H-atoms coordinates and complete geometry can be obtained on request.

RESULTS AND DISCUSSION

The crystal used for the structure determination was obtained by slow evaporation from ethanol. The structure was solved by direct methods using SHELXTL-Plus package (PC version),[7] and refined by least-squares using SHELXS-93 program.[8]

All H-atoms were located at calculated idealized positions based on the molecular geometry with C-H = 0.96 Å. These positions were constrained during the subsequent refinement. In final cycles of refinement, thermal parameters for all H atoms were constrained to the equivalent isotropic temperature factor of the C atoms to which they were bonded.

Atomic coordinates of each independent molecule was obtained from crystallographic studies (Table I). Atomic geometrical parameters (Tables II and III) describing the two possible conformations of (II) are in agreement with the mean values reported.[9] The thermal ellipsoids of the molecules with the atomic numbering (SHELXTL-Plus)[7] are shown in figure 1. A projection of the title compound (short intermo-lecular contacts between Br-O atoms are denoted by dashed lines) can be found in figure 2.

TABLE I
Atom coordinates (· 10^4) and temperature factors (Å^2 · 10^3) for $C_7H_6NO_3Br$

Atom	x	y	z	Ui,j
Br(1)	2884(2)	-870(1)	4749(1)	60(1)*
O(1)a	2703(8)	-3399(5)	4810(5)	44(2)*
C(2)a	3333(11)	-2413(7)	4053(8)	42(3)*
C(3)a	4146(13)	-2764(8)	2884(9)	54(4)*
C(4)a	4044(13)	-4070(8)	2900(9)	51(4)*
C(5)a	3191(12)	-4432(8)	4075(8)	43(3)*
C(6)a	2739(12)	-5637(8)	4599(9)	48(4)*
C(7)a	1904(12)	-5989(8)	5792(9)	46(4)*
C(8)a	1194(14)	-5229(8)	6883(9)	57(4)*
N(1)a	1640(12)	-7318(8)	6016(11)	63(4)*
O(2)a	1053(13)	-7708(8)	7086(9)	98(4)*
O(3)a	2087(14)	-8018(7)	5132(9)	100(4)*
Br(2)	2248(1)	3658(1)	330(1)	58(1)*
O(1)b	2323(7)	1112(5)	198(5)	42(2)*
C(2)b	1679(11)	2063(8)	1016(8)	43(3)*
C(3)b	796(13)	1680(8)	2142(9)	49(4)*
C(4)b	802(12)	372(8)	2075(8)	45(3)*
C(5)b	1731(12)	38(8)	909(8)	42(3)*
C(6)b	2127(11)	-1144(8)	360(8)	43(3)*
C(7)b	3080(11)	-1449(7)	-807(9)	42(3)*
C(8)b	3978(13)	-617(9)	-1869(9)	56(4)*
N(1)b	3236(11)	-2765(8)	-1080(10)	60(4)*
O(2)b	2642(13)	-3532(7)	-228(9)	92(4)*
O(3)b	3945(12)	-3055(7)	-2142(9)	87(4)*

* Equivalent isotropic U defined as one third of the trace of the orthogonalised U(i,j) tensor.

TABLE II
Bond lengths (Å) and bond angles (°)f or $C_7H_6NO_3Br$

Bond	Distance	Bond	Distance
Br(1)-C(2)a	1.842(8)	O(1)a-C(2)a	1.351(9)
O(1)a-C(5)a	1.39(1)	C(2)a-C(3)a	1.34(1)
C(3)a-C(4)a	1.42(1)	C(4)a-C(5)a	1.34(1)
C(5)a-C(6)a	1.42(1)	C(6)a-C(7)a	1.35(1)
C(7)a-C(8)a	1.45(1)	C(7)a-N(1)a	1.46(1)
N(1)a-O(2)a	1.20(1)	N(1)a-O(3)a	1.23(1)
Br(2)-C(2)b	1.872(8)	O(1)b-C(2)b	1.38(1)
O(1)b-C(5)b	1.40(1)	C(2)b-C(3)b	1.31(1)
C(3)b-C(4)b	1.41(1)	C(4)b-C(5)b	1.35(1)
C(5)b-C(6)b	1.42(1)	C(6)b-C(7)b	1.35(1)
C(7)b-C(8)b	1.48(1)	C(7)b-N(1)b	1.46(1)
N(1)b-O(2)b	1.23(1)	N(1)b-O(3)b	1.20(1)
Atoms	Angle	Atoms	Angle
C(2)a-O(1)a-C(5)a	106.2(6)	Br(1)-C(2)a-O(1)a	117.2(6)
Br(1)-C(2)a-C(3)a	131.8(7)	O(1)a-C(2)a-C(3)a	110.9(7)
C(2)a-C(3)a-C(4)a	106.4(8)	C(3)a-C(4)a-C(5)a	107.1(8)
O(1)a-C(5)a-C(4)a	109.3(7)	O(1)a-C(5)a-C(6)a	120.5(7)
C(4)a-C(5)a-C(6)a	130.2(8)	C(5)a-C(6)a-C(7)a	129.4(9)
C(6)a-C(7)a-C(8)a	129.2(8)	C(6)a-C(7)a-N(1)a	115.3(9)
C(8)a-C(7)a-N(1)a	115.5(8)	C(7)a-N(1)a-O(2)a	118.1(10)
C(7)a-N(1)a-O(3)a	120.1(9)	O(2)a-N(1)a-O(3)a	121.7(9)

TABLE III
Selected torsion angles (°)

Molec ule A					Molec ule B				
Atoms				Angle	Atoms				Angle
C5A	O1A	C2A	BR1	179.4(0.6)	C5B	O1B	C2B	BR2	-179.7(0.6)
C5A	O1A	C2A	C3A	1.4(1.0)	C5B	O1B	C2B	C3B	1.1(1.0)
C2A	O1A	C5A	C4A	-1.7(1.0)	C2B	O1B	C5B	C4B	-0.2(1.0)
C2A	O1A	C5A	C6A	179.4(0.8)	C2B	O1B	C5B	C6B	179.1(0.8)
BR1	C2A	C3A	C4A	-178.3(0.8)	BR2	C2B	C3B	C4B	179.5(0.8)
O1A	C2A	C3A	C4A	-0.6(1.1)	O1B	C2B	C3B	C4B	-1.5(1.1)
C2A	C3A	C4A	C5A	-0.4(1.2)	C2B	C3B	C4B	C5B	1.3(1.1)
C3A	C4A	C5A	O1A	1.3(1.1)	C3B	C4B	C5B	O1B	-0.7(1.1)
C3A	C4A	C5A	C6A	-179.9(1.0)	C3B	C4B	C5B	C6B	-179.8(1.0)
O1A	C5A	C6A	C7A	-2.5(1.5)	O1B	C5B	C6B	C7B	1.8(1.5)
C4A	C5A	C6A	C7A	178.9(1.1)	C4B	C5B	C6B	C7B	-179.1(1.0)
C5A	C6A	C7A	C8A	1.1(1.8)	C5B	C6B	C7B	C8B	-0.9(1.7)
C5A	C6A	C7A	N1A	179.8(0.9)	C5B	C6B	C7B	N1B	-179.9(0.9)
C6A	C7A	N1A	O2A	173.5(1.0)	C6B	C7B	N1B	O2B	-5.8(1.4)
C6A	C7A	N1A	O3A	-3.5(1.4)	C6B	C7B	N1B	O3B	174.1(0.9)
C8A	C7A	N1A	O2A	-7.6(1.4)	C8B	C7B	N1B	O2B	175.1(0.9)
C8A	C7A	N1A	O3A	175.4(1.0)	C8B	C7B	N1B	O3B	-5.0(1.3)

In the title compound (II), asfound in compound (I), the molecule in the crystal is essentially planar and all atoms lie in the plane defined by the furanic ring. In compound (II), there are two crystallographically independent but chemically equivalent molecules present in the asymmetric unit. The mean Br-C2 bond lengths in (II) is significantly

shorter [1.854(8) Å] than the reported mean value of 1.88(2) Å for Br-C bonds in (I). The other bond lengths and angles are in agreement with those reported in the previous analogue structure.[3]

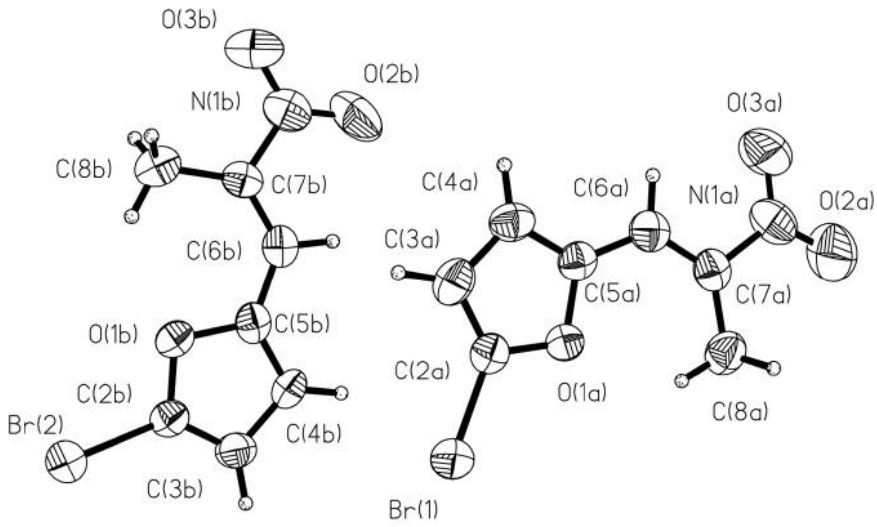

Fig. 1. A perspective view of the molecules, present in the asymmetry unit, with the numbering scheme. (SHELXTL-Plus).[7] Ellipsoids are scaled to enclose 50 % probability. H-atoms are represented as spheres of arbitrary radii.

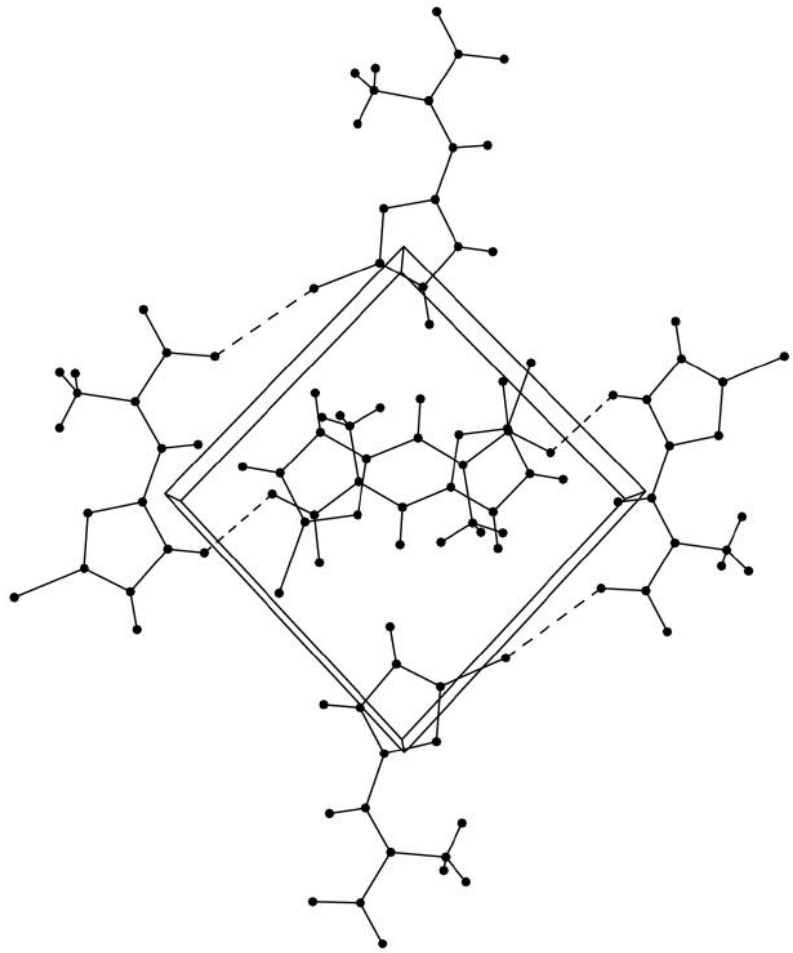

Fig. 2. Packing of molecules in the unit cell, a short intermolecular contact between Br-O atoms (mean value = 3.08 Å, [3.08 Å < WrBr + WrO - 0.2 Å] is denoted by dashed lines (Wr is the van der Waals radii for the corresponding atom).

The C-H···O intramolecular and intermolecular interactions for (II) are reported in Table IV. The structures are both stabilized by these interactions and by van der Waals forces. The closest intermolecular contact between non-H atoms is 3.072(7)Å for Br(2)···O(2)b, and the closest of such contact between non-H atoms is 2.56(1)Å for O(2)a···H(4)b.

TABLE IV
Intermolecular and intramolecular short contacts

Donor-H	Donor····Acceptor	H···Acceptor	Donor-H···Acceptor
C8a-H8a	C8a···O1a (i)	H8a···O1a (i)	C8a-H8a···O1a (i)
0.960(.013)	2.976(.010)	2.238(.010)	132.95(0.92)
1.080		2.158	130.62(**)
C8b-H8d	C8b···O1b (i)	H8d···O1B (i)	C8b-H8d···O1b (i)
0.960(.014)	2.974(.011)	2.235(.010)	132.99(0.93)
1.080		2.155	130.66(**)
C6a-H6a	C6a···O3b (ii)	H6a···O3b (ii)	C6a-H6a···O3ab(ii)
0.960(.013)	3.429(.012)	2.685(.011)	134.70(0.92)
1.080		2.602	132.82(**)
C4a-H4a	C4a···O3b (ii)	H4a···O3b (ii)	C4a-H4a···O3b (ii)
0.960(.013)	3.322(.011)	2.623(.011)	129.92(0.88)
1.080		2.548	127.85(**)
C6b-H6b	C6b···O2a (iii)	H6b···O2a (iii)	C6b-H6b···O2a (iii)
0.960(.012)	3.451(.012)	2.652(.012)	141.01(0.87)
1.080		2.559	139.32(**)
C4b-H4b	C4b···O2a (iii)	H4b···O2a (iii)	C4b-H4b···O2a (iii)
0.960(.012)	3.317(.012)	2.560(.013)	135.81(0.87)
1.080		2.476	133.87(**)

Equivalent positions: (i) x,y,z. (ii) -x+1,-y-1,-z. (iii) -x,-y-1,-z+1.
(**) Values normalized.[10,11]

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