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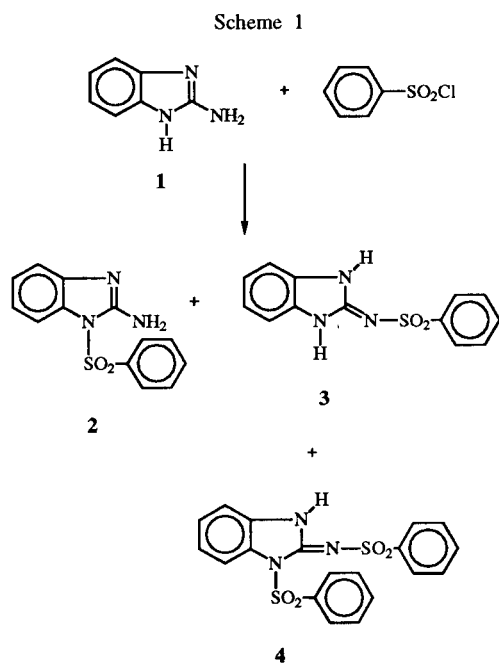
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A number of benzenesulfonyl derivatives of benzoimidazol-2-ylamine and 1-methyl-benzoimidazol-2-ylamine were synthesized, their synthesis reactions under different experimental conditions being monitored by hptlc. The crystal and molecular structures of *N*-(1-benzenesulfonyl-1,3-dihydrobenzoimidazol-2-ylidene)benzenesulfonamide (**4**) and *N*-(1-benzenesulfonyl-3-methyl-1,3-dihydro-benzoimidazol-2-ylidene)-benzenesulfonamide (**7**) were determined by X-ray diffraction analysis. The structure of compound **4** is made up of two crystallographically independent molecules and that of compound **7** of one molecule. In both cases, the structure contains the imido form of the molecules. There are strong conjugative effects between the imido groups and the imidazolic rings. Weak intramolecular C-H...O hydrogen bonding interactions could influence the molecular conformations.

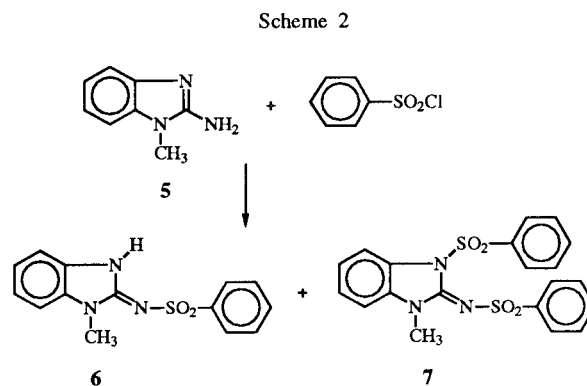
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Benzoimidazole derivatives are an important class of heterocyclic compounds which have anticonvulsant [1], sedative [2], immunosuppressive [3], antitumor [4], antihistaminic [5], antifungal [6] and anthelmintic activity [7].

The aim of this study was to synthesize benzenesulfonyl derivatives of 1*H*-benzoimidazol-2-ylamine (**1**) and of 1-methyl-1*H*-benzoimidazol-2-ylamine (**5**) to determine their chemical and physical parameters, and to determine the crystal and molecular structure of compounds which gave crystals suitable for X-ray analysis **4** and **7**.



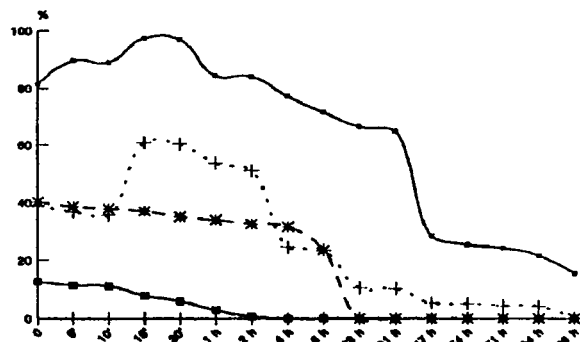
For this purpose, we prepared **2**, **3**, **4** and **6**, **7**, respectively by reaction of **1** (Scheme 1) and of **5** (Scheme 2) with benzenesulfonyl chloride. The compounds were separated out by dissolving them in alkali or by medium-pressure liquid chromatography (mpc).



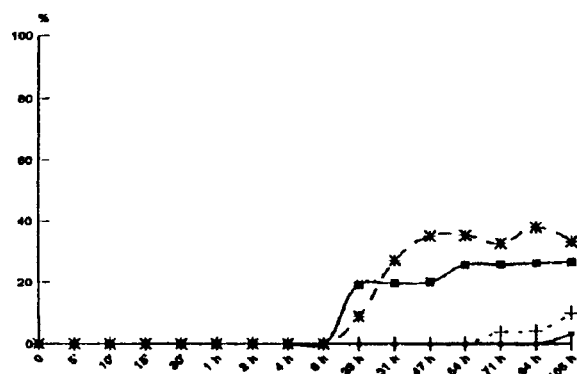
The reactions at different temperatures and with different amounts of benzenesulfonyl chloride, were monitored by means of a high-performance thin-layer chromatographic technique (hptlc). The identity of the compounds obtained was verified on the basis of their R_f values and by means of a computerized identity check, whereby their uv spectra, obtained by scanning the hptlc plate, were compared with standard spectra.

The results for **1** (Graph 1) show the formation of compound **2**, **4** and **3** in that order. Compound **2** is obtained in highest yield after a short time under mild conditions (1 equivalent 25°), while compound **4** requires 2 equivalents at 25°. Compound **3** is only obtained with 1 equivalent at 50° after a long time.

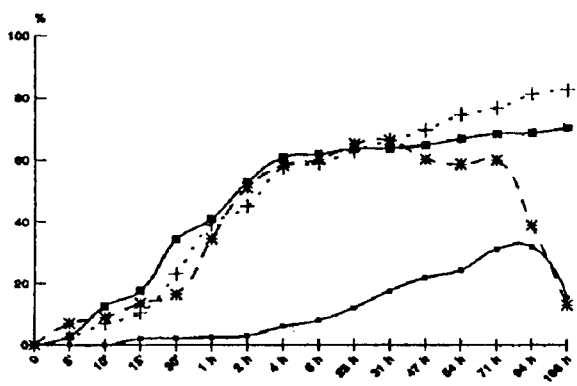
compound 2



compound 3



compound 4

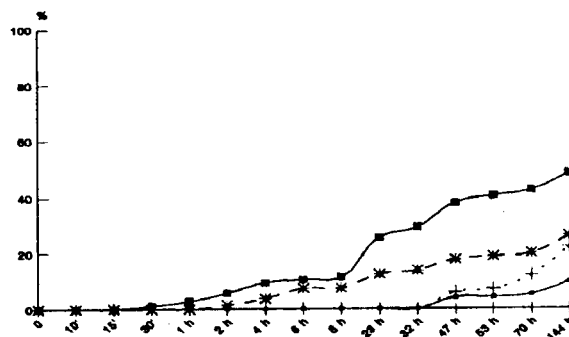


Graph 1. Reaction of compound 1 with benzenesulfonyl chloride.

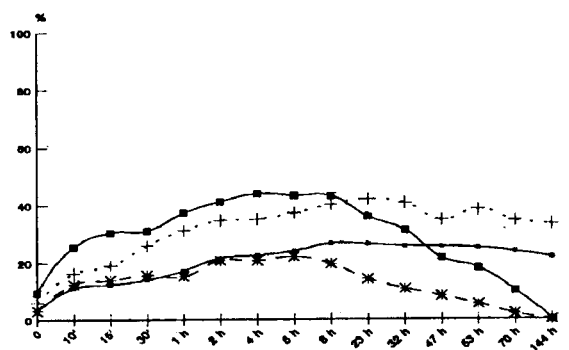
experimental conditions
 → 1 equiv 25°C + 2 equiv 25°C * 1 equiv 50°C ■ 2 equiv 50°C

The results for 5 (Graph 2) show the formation of 7 and then of 6. Compound 7 is obtained in a high yield with 2 equivalents at 25° after 23 hours, whereas 6 is obtained with 2 equivalents at 50° after one week.

compound 6



compound 7



Graph 2. Reaction of compound 5 with benzenesulfonyl chloride.

experimental conditions
 → 1 equiv 25°C + 2 equiv 25°C * 1 equiv 50°C ■ 2 equiv 50°C

Description of Crystal Structures of 4 and 7.

The asymmetric unit of compound 4 contains two crystallographically-independent molecules, illustrated in Figure 1, whereas the crystal structure of compound 7 is made up of one independent molecule, depicted in Figure 2. Selected geometrical parameters for both compounds are given in Table 1, and probable hydrogen bonding interactions are listed in Table 2.

Our structural determinations afford experimental evidence of the imido nature of the hexocyclic N(4) atom in both compounds. This involves, at least for compound 4, the transfer of one amide hydrogen atom to the unprotonated nitrogen of the imidazole ring. It is interesting to note that the same type of proton transfer (to a pyridyl or pyrimidinyl nitrogen) was previously observed in other *N*-heteroaromatic sulfonamides, such as: ethyl 3-[4,5-dimethoxy-2-(4-methyl-2-pyridylsulfamoyl)phenyl]propionate [8], sulfapyridine [9,10] and sulfamethomidine in a solvate form [8]. As previously

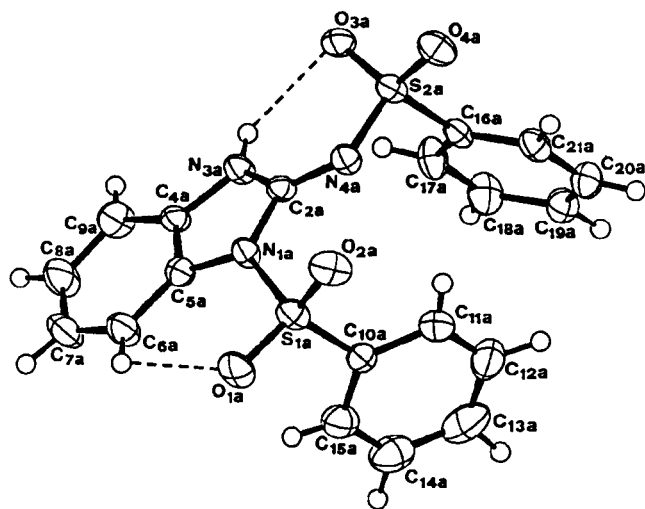


Figure 1. ORTEP [21] drawing of the two crystallographically independent molecules of compound 4 with atom numbering scheme. Thermal ellipsoids for non-H atoms enclose 40% probability. Dashed lines represent intramolecular hydrogen bonds.

pointed out [9,12], the C-N and N-S bonds of imido fragments display considerable amount of double-bond character and are significantly shorter than those of the corresponding amido forms. The N(4)-S(2) bond distances, which range from 1.589 (2) to 1.599 (3) Å, are in good agreement with those observed in the above cited compounds (range 1.582 (4)-1.628 (4) Å), but we observe markedly shorter C(2)-N(4) bond lengths, in the 1.303 (3) -1.319 (4) Å interval, which compare with values ranging from 1.339 (6) [11] to 1.359 (6) Å [8]. The shortening of our C-N bonds could be due to conjugative effects between the imido groups and the imidazolic rings, which appear stronger than those with pyridine cycles. It should also be pointed out that,

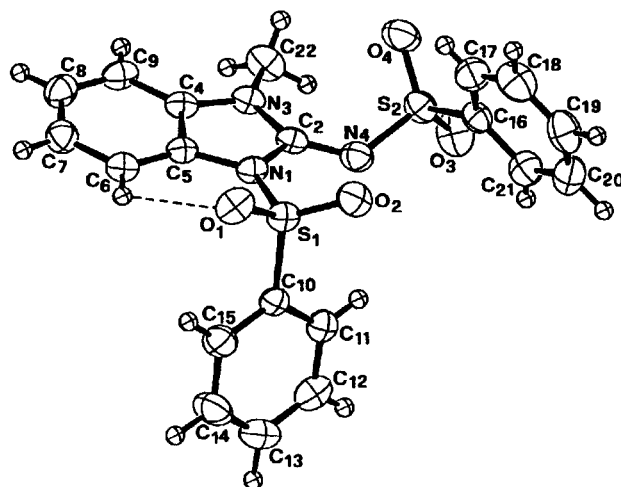


Figure 2. The molecular structure of compound 7 with atom numbering scheme. Thermal ellipsoids for non-H atoms are drawn at 40% probability.

because of the fundamental sp^2 character of the imido N atom and the strong double-bond order of its bonds, C(2)-N(4)-S(2) bond angles close to 120° and a nearly coplanar arrangement of the N(3)-C(2)-N(4)-S(2) fragment would be expected. However, this was observed

Table 1
Selected Bond Distances (Å), Bond Angles (deg) and Torsion Angles (deg)

	Compound 4		Compound 7
	mol. a	mol. b	
C(2)-N(1)	1.392 (4)	1.398 (5)	1.396 (3)
C(5)-N(1)	1.429 (4)	1.422 (5)	1.414 (3)
S(1)-N(1)	1.708 (3)	1.700 (3)	1.700 (2)
N(3)-C(2)	1.338 (4)	1.335 (5)	1.354 (3)
N(4)-C(2)	1.319 (4)	1.307 (4)	1.303 (3)
C(4)-N(3)	1.403 (4)	1.386 (5)	1.387 (3)
C(5)-C(4)	1.380 (5)	1.377 (5)	1.393 (3)
O(1)-S(1)	1.416 (3)	1.416 (3)	1.422 (2)
O(2)-S(1)	1.410 (3)	1.408 (3)	1.413 (2)
C(10)-S(1)	1.740 (4)	1.728 (5)	1.753 (3)
S(2)-N(4)	1.599 (3)	1.598 (3)	1.589 (2)
O(3)-S(2)	1.442 (3)	1.445 (3)	1.434 (2)
O(4)-S(2)	1.433 (3)	1.429 (3)	1.440 (2)
C(16)-S(2)	1.758 (4)	1.759 (4)	1.762 (3)
C(22)-N(3)	—	—	1.458(3)
C(5)-N(1)-C(2)	107.9 (3)	108.4 (3)	109.6 (2)
S(1)-N(1)-C(2)	123.0 (2)	123.5 (3)	125.9 (2)
S(1)-N(1)-C(5)	125.0 (2)	127.8 (3)	124.4 (2)
N(3)-C(2)-N(1)	107.5 (3)	106.8 (3)	106.4 (2)
N(4)-C(2)-N(1)	120.6 (3)	120.4 (3)	122.3 (2)
N(4)-C(2)-N(3)	131.9 (3)	132.7 (3)	131.0 (2)
C(4)-N(3)-C(2)	110.8 (3)	110.9 (3)	110.3 (2)
C(22)-N(3)-C(2)	—	—	125.8 (2)
C(22)-N(3)-C(4)	—	—	123.5 (2)
C(5)-C(4)-N(3)	106.9 (3)	107.8 (3)	108.4 (2)
C(4)-C(5)-N(1)	106.8 (3)	106.0 (3)	105.2 (2)
O(1)-S(1)-N(1)	103.8 (2)	103.6 (2)	104.4 (1)
O(2)-S(1)-N(1)	106.9 (2)	107.3 (2)	107.0 (1)

Table 1 (continued)

	Compound 4		Compound 7
	mol. a	mol. b	
O(2)-S(1)-O(1)	120.9 (2)	120.4 (2)	120.7 (1)
C(10)-S(1)-N(1)	102.5 (2)	103.0 (2)	102.7 (1)
C(10)-S(1)-O(1)	110.3 (2)	110.1 (2)	109.1 (1)
C(10)-S(1)-O(2)	110.6 (2)	110.6 (2)	111.0 (1)
S(2)-N(4)-C(2)	121.6 (3)	122.3 (3)	127.9 (2)
O(3)-S(2)-N(4)	111.5 (2)	112.5 (2)	108.8 (1)
O(4)-S(2)-N(4)	107.5 (2)	107.9 (2)	112.9 (1)
O(4)-S(2)-O(3)	116.7 (2)	116.4 (2)	117.4 (1)
C(16)-S(2)-N(4)	104.7 (2)	103.6 (2)	103.1 (1)
C(16)-S(2)-O(3)	107.8 (2)	107.0 (2)	106.6 (1)
C(16)-S(2)-O(4)	107.9 (2)	108.7 (2)	106.9 (1)
C(2)-N(1)-S(1)-O(1)	179.7 (3)	-176.9 (3)	151.3 (2)
C(2)-N(1)-S(1)-O(2)	50.8 (3)	54.7 (3)	22.2 (2)
C(2)-N(1)-S(1)-C(10)	-65.5 (3)	-62.1 (3)	-94.8 (2)
C(5)-N(1)-S(1)-O(1)	-25.9 (4)	-4.6 (4)	-24.1 (2)
C(5)-N(1)-S(1)-O(2)	-154.8 (3)	-133.0 (3)	-153.1 (2)
C(5)-N(1)-S(1)-C(10)	89.8 (2)	88.9 (3)	110.2 (3)
S(1)-N(1)-C(2)-N(4)	-20.0 (5)	-7.7 (5)	-13.5 (4)
N(1)-C(2)-N(4)-S(2)	176.7 (3)	172.7 (3)	-139.0 (2)
N(3)-C(2)-N(4)-S(2)	-2.2 (6)	-9.0 (6)	48.7 (4)
C(2)-N(4)-S(2)-O(3)	26.0 (3)	13.6 (4)	-129.4 (2)
C(2)-N(4)-S(2)-O(4)	155.0 (3)	143.3 (3)	2.8 (3)
C(2)-N(4)-S(2)-C(16)	-90.4 (3)	-101.6 (3)	117.8 (2)
N(1)-S(1)-C(10)-C(11)	92.5 (4)	102.4 (4)	77.4 (2)
N(1)-S(1)-C(10)-C(15)	-84.9 (4)	-77.5 (5)	-102.0 (2)
N(4)-S(2)-C(16)-C(17)	82.5 (4)	78.9 (4)	-91.6 (2)
N(4)-S(2)-C(16)-C(21)	-96.8 (3)	-100.7 (3)	88.1 (2)

only in the two independent molecules of compound **4** (see Table 1); in compound **7** the bond angle at N(4) is widened to 127.9 (2)° and the N(3)-C(2)-N(4)-S(2) torsion angle is 48.7 (4)°. These deviations from the expected geometry may be due to steric hindrance between the sulfonic oxygens and the methyl substituent at the N(3) atom. Furthermore, this appears to be the most significant structural difference existing between the two independent molecules of compound **4** and that of compound **7**, whose dimensions are in very good agreement. It is also worth noting the marked lengthening of the N-S bonds between sulfonic groups bonded to N(1) ring atoms with respect to those bonded to imido nitrogens (about 0.10 Å). The S(1)-C(1) bond distances (from 1.700 (2) to 1.708 (3) Å) are quite close to the calculated values of 1.73-1.74 Å for S-N pure single bonds [13,14], and agree well with the value of 1.708 (3) Å found in 1-mesitylsulfonyl-4-nitroimidazole [15]. This C-S bond lengthening is accompanied by a significant increase in the double bond character of the adjacent S-O bonds. In our three molecules, the S(1)-O bond lengths range from 1.408 (3) to 1.422 (2) Å with a mean value of 1.414 (3), whereas the mean value of S(2)-O bond lengths is 1.437 (3) and their range 1.429 (3)-1.445 (3) Å. As previously observed [8,12], the tetrahedral coordination around the S atoms is severely distorted in this case as well (see Table 1), with the

largest deformations occurring at O(1)-S(1)-O(2) bond angles, all of which are greater than 120°.

Comparison between the dimensions of our benzimidazole moieties and those of the benzimidazole molecule [16,17] shows significant lengthening of some bond distances within the imidazole ring. Our C(5)-N(1), N(1)-C(2), and C(2)-N(3) distances are all longer (about 0.03 Å) than the corresponding values reported for the unsubstituted molecule. This seems to be due to the electron-withdrawing ability of the benzenesulfonyl groups, and primarily to that bonded to imido nitrogen, owing to its strong conjugative effects. It appears perhaps significant that this bond lengthening is accompanied by relevant deviations from the coplanarity of benzoimidazole atoms, not observed in previous structural reports [16,17]. The largest atomic deviations from mean least-squares planes are 0.014 and 0.032 Å, respectively, in the *a* and *b* molecules of compound **4**, and 0.033 in that of compound **7**; the atoms bonded to the imidazole rings display much more relevant deviations from these planes, the largest being that of the S (1a) atom of 0.489 Å.

The orientations of the benzenesulfonyl groups with respect to the imidazole ring to which they are bonded could be determined not only by intramolecular hydrogen-bonding interactions involving sulfonic oxygens and N- but also by C-bonded hydrogen atoms (see Table 2 and

Table 2
Probable Hydrogen Bonding Interactions

1	atoms		1...3	1—2	2...3	∠1-2...3
	2	3				
in Compound 4						
a) intramolecular						
N(3a)	H(N3a)	...O(3a)	2.772 (3)	0.89	2.26	117
C(6a)	H(6a)	...O(1a)	2.898 (6)	0.90	2.39	116
N(3b)	H(N3b)	...O(3b)	2.746 (3)	0.82	2.18	125
C(6b)	H(6b)	...O(1b)	2.912 (7)	0.94	2.29	123
b) intermolecular						
N(3a)	H(N3a)	...O(3b)	2.969 (5)	0.89	2.12	160
N(3b)	H(N3b)	...O(3a)	2.803 (5)	0.82	2.13	146
in Compound 7						
a) intramolecular						
C(6)	H(6)	...O(1)	2.931 (3)	0.88	2.46	114

Figures 1 and 2). Our C-H...O bond distances and angles, in both compounds, are consistent with those reported by Taylor and Kennard [18] for this type of a fairly rare interaction. The orientations of the benzene rings, which are roughly normal to the benzoimidazole planes, appear determined by crystal packing requirements. One of them, that bonded to the S (1b) atom, is slightly disordered, as shown by the large thermal motion parameters of some of its carbon atoms (see Figure 1).

The molecular packing of compound **4** is characterized by only a few short van der Waals contacts, mainly involving sulfonic oxygen atoms. In compound **7**, the two crystallographically-independent molecules are tied as dimeric pairs by two fairly strong N-H...O hydrogen bonding interactions (see Table 2) and are hence involved in bifurcated, intra- and inter-molecular, hydrogen bonding. These dimeric units are separated, as in compound **4**, by a few short van der Waals contacts.

Table 3
Crystallographic Data

	Compound 4	Compound 7
Formula	C ₁₉ H ₁₅ N ₃ O ₄ S ₂	C ₂₀ H ₁₇ N ₃ O ₄ S ₂
Molecular Weight	413.477	427.503
Crystal System [a]	triclinic	monoclinic
Space Group	P1 (No. 2)	P2 ₁ /c (No. 14)
a, Å	8.270 (2)	9.890 (2)
b, Å	15.139 (3)	15.164 (3)
c, Å	15.982 (3)	12.715 (2)
α, deg	73.50 (2)	90
β, deg	75.38 (2)	96.99 (2)
γ, deg	81.47 (2)	90
V, Å ³	1850 (2)	1892.7 (8)
Z	4	4
D _{calcd} , g·cm ⁻³	1.481	1.500
F (000)	856	888
Radiation (λ, Å)	Graphite-monochromated	MoKα
Reflection measured	±h, ±k, +l	±h, +k, +l
Scan Type	ω-2θ	ω-2θ
θ limits, deg	2.0-27.0	2.0-26.0
Scan Width, deg	0.80+0.35 tanθ	0.65+0.35 tanθ
Scan Speed limits, deg·min ⁻¹	1.27-4.12	1.00-5.50
Standard Reflections	2 every 3h (no changes)	2 every 3h (no changes)
No. of measured Reflections	8628	3892
No. of observed Reflections	3784 with I > 2σ(I)	2302 with I > 3σ(I)
No. of independent Reflections	3308 (R _{int} = 0.014)	2184 (R _{int} = 0.018)
Crystal Dimensions, mm	0.28 x 0.20 x 0.10	0.31 x 0.25 x 0.18
μ, cm ⁻¹	2.69	2.64
Transmission, max-min	0.998-0.906	0.999-0.941
No. of Varied Parameters	505	262
R	0.036	0.033
R _w	0.038	0.037
w	1.07/[σ ² (F _o)+0.0008F _o ²]	1.0/[σ ² (F _o)+0.000963F _o ²]
G.o.F	1.18	1.27
Δρ, max-min, e·Å ⁻³	+0.23-0.24	+0.20-0.29
Secondary Extinction	no evidence	0 weight to 3 strong low-order reflections

[a] Unit cell parameter were derived from least-squares fit to the setting angles of 25 intense reflections from various regions of reciprocal space.

Table 4
Final Fractional Coordinates and Equivalent Isotropic Temperature Factors [a] for the Non-hydrogen Atoms of the *N*-(1-Benzene-sulfonyl-1,3-dihydrobenzoimidazol-2-ylidene)benzenesulfonamide (**4**)

atom	x	y	z	B _{eq} , Å ²
N(1a)	0.2507 (4)	0.8154 (2)	-0.0060 (2)	2.7 (1)
C(2a)	0.2909 (5)	0.7657 (3)	0.0749 (2)	2.5 (2)
N(3a)	0.3087 (4)	0.8269 (2)	0.1174 (2)	3.0 (1)
C(4a)	0.2833 (5)	0.9177 (3)	0.0659 (2)	2.8 (2)
C(5a)	0.2476 (5)	0.9116 (2)	-0.0119 (3)	2.7 (2)
C(6a)	0.2140 (6)	0.9894 (3)	-0.0764 (3)	3.8 (2)
C(7a)	0.2196 (7)	1.0733 (3)	-0.0588 (3)	4.8 (2)
C(8a)	0.2543 (7)	1.0790 (3)	0.0183 (3)	5.0 (2)
C(9a)	0.2849 (6)	1.0007 (3)	0.0836 (3)	4.3 (2)
S(1a)	0.2794 (1)	0.76944 (7)	-0.09525 (7)	3.03 (4)
O(1a)	0.2218 (4)	0.8428 (2)	-0.1613 (2)	4.1 (1)
O(2a)	0.2038 (4)	0.6851 (2)	-0.0631 (2)	4.0 (1)
C(10a)	0.4966 (5)	0.7498 (3)	-0.1245 (2)	2.8 (2)
C(11a)	0.5759 (6)	0.6650 (3)	-0.0896 (3)	4.0 (2)
C(12a)	0.7467 (7)	0.6536 (4)	-0.1108 (4)	5.7 (3)
C(13a)	0.8375 (7)	0.7243 (5)	-0.1660 (4)	5.9(3)
C(14a)	0.7592 (7)	0.8077 (4)	-0.2010 (3)	5.2 (3)
C(15a)	0.5902 (6)	0.8207 (3)	-0.1801 (3)	4.0 (2)
N(4a)	0.3067 (4)	0.6745 (2)	0.0964 (2)	2.8 (1)
S(2a)	0.3622 (1)	0.61601 (6)	0.18655 (6)	2.74 (4)
O(3a)	0.3186 (3)	0.6668 (2)	0.2541 (2)	3.3 (1)
O(4a)	0.2989 (4)	0.5270 (2)	0.2105 (2)	3.8 (1)
C(16a)	0.5821 (5)	0.6008 (2)	0.1560 (2)	2.7 (2)
C(17a)	0.6792 (6)	0.6705 (3)	0.1522 (3)	3.9 (2)
C(18a)	0.8488 (6)	0.6577 (3)	0.1273 (3)	4.5 (2)
C(19a)	0.9270 (5)	0.5780 (3)	0.1061 (3)	3.9 (2)
C(20a)	0.8306 (6)	0.5094 (3)	0.1113 (3)	3.9 (2)
C(21a)	0.6593 (5)	0.5207 (2)	0.1350 (3)	3.1 (2)
N(1b)	0.3114 (4)	0.7047 (2)	0.5542 (2)	3.1 (1)
C(2b)	0.3542 (5)	0.7473 (3)	0.4626 (2)	2.6 (2)
N(3b)	0.3450 (4)	0.6848 (2)	0.4198 (2)	3.2 (1)
C(4b)	0.2965 (5)	0.6022 (3)	0.4801 (3)	3.3 (2)
C(5b)	0.2757 (5)	0.6125 (3)	0.5651 (3)	3.1 (2)
C(6b)	0.2204 (7)	0.5420 (3)	0.6398 (3)	4.5 (2)
C(7b)	0.1909 (8)	0.4622 (3)	0.6233 (3)	5.7 (3)
C(8b)	0.2129 (8)	0.4517 (3)	0.5390 (4)	6.1 (3)
C(9b)	0.2666 (7)	0.5213 (3)	0.4653 (3)	5.0 (2)
S(1b)	0.3248 (1)	0.75453 (7)	0.63480 (7)	3.36 (5)
O(1b)	0.2786 (4)	0.6852 (2)	0.7153 (2)	5.4 (2)
O(2b)	0.2313 (4)	0.8410 (2)	0.6204 (2)	4.4 (1)
C(10b)	0.5363 (5)	0.7685 (3)	0.6129 (3)	3.7 (2)
C(11b)	0.5942 (7)	0.8541 (4)	0.5701 (3)	5.0 (2)
C(12b)	0.764 (1)	0.8615 (6)	0.5534 (4)	8.6 (4)
C(13b)	0.872 (1)	0.786 (1)	0.5774 (7)	12.9 (9)
C(14b)	0.806 (1)	0.7064 (8)	0.6187 (7)	10.9 (7)
C(15b)	0.6448 (8)	0.6929 (4)	0.6388 (4)	6.5 (3)
N(4b)	0.3899 (4)	0.8335 (2)	0.4346 (2)	2.8 (1)
S(2b)	0.4600 (1)	0.88192 (6)	0.33135 (7)	2.73 (4)
O(3b)	0.4415 (3)	0.8284 (2)	0.2730 (2)	3.4 (1)
O(4b)	0.3887 (4)	0.9755 (2)	0.3137 (2)	4.2 (1)
C(16b)	0.6762 (5)	0.8817 (3)	0.3229 (3)	2.8 (2)
C(17b)	0.7761 (6)	0.8021 (3)	0.3187 (3)	4.4 (2)
C(18b)	0.9435 (7)	0.8009 (4)	0.3129 (4)	6.1 (3)
C(19b)	1.0095 (6)	0.8809 (5)	0.3102 (4)	6.5 (3)
C(20b)	0.9086 (7)	0.9595 (4)	0.3152 (3)	5.3 (3)
C(21b)	0.7402 (5)	0.9617 (3)	0.3211 (3)	3.6 (2)

[a] B_{eq} is defined as one-third of the trace of the orthogonalized B_{ij} tensor.

Table 5

Final Fractional Coordinates and Equivalent Isotropic Temperature Factors [a] for the Non-hydrogen Atoms of the *N*-(1-Benzenesulfonyl-3-methyl-1,3-dihydrobenzimidazol-2-ylidene)benzenesulfonamide (7)

atom	x	y	z	B _{eq} , Å ²
N(1)	0.0390 (2)	0.5469 (1)	0.2812 (2)	3.09 (8)
C(2)	0.1766 (3)	0.5340 (2)	0.3176 (2)	3.1 (1)
N(3)	0.1826 (2)	0.4631 (1)	0.3829 (2)	3.33 (8)
C(4)	0.0525 (3)	0.4325 (2)	0.3923 (2)	3.2 (1)
C(5)	-0.0408 (3)	0.4855 (2)	0.3304 (2)	3.1 (1)
C(6)	-0.1789 (3)	0.4726 (2)	0.3266 (2)	3.6 (1)
C(7)	-0.2218 (3)	0.4036 (2)	0.3851 (2)	4.3 (1)
C(8)	-0.1296 (3)	0.3498 (2)	0.4460 (2)	4.5 (1)
C(9)	0.0081 (3)	0.3634 (2)	0.4512 (2)	4.0 (1)
N(4)	0.2708 (2)	0.5889 (2)	0.2962 (2)	4.0 (1)
S(1)	-0.02441 (7)	0.61961 (4)	0.18611 (5)	3.35 (3)
O(1)	-0.1482 (2)	0.5805 (1)	0.1397 (1)	4.53 (8)
O(2)	0.0814 (2)	0.6383 (1)	0.1241 (1)	4.62 (9)
C(10)	-0.0620 (2)	0.7120 (2)	0.2601 (2)	3.07 (9)
C(11)	0.0438 (3)	0.7665 (2)	0.3017 (2)	3.7 (1)
C(12)	0.0122 (3)	0.8380 (2)	0.3614 (2)	4.6 (1)
C(13)	-0.1191 (4)	0.8557 (2)	0.3770 (3)	5.0 (1)
C(14)	-0.2231 (3)	0.8016 (2)	0.3352 (3)	5.6 (2)
C(15)	-0.1944 (3)	0.7279 (2)	0.2761 (2)	4.5 (1)
S(2)	0.41776 (7)	0.56642 (5)	0.26506 (5)	3.88 (3)
O(3)	0.5172 (2)	0.6165 (2)	0.3316 (2)	5.6 (1)
O(4)	0.4412 (2)	0.4731 (1)	0.2565 (2)	5.4 (1)
C(16)	0.4129 (2)	0.6107 (2)	0.1365 (2)	3.5 (1)
C(17)	0.3724 (3)	0.5589 (2)	0.0496 (2)	4.7 (1)
C(18)	0.3690 (4)	0.5925 (3)	-0.0516 (3)	5.7 (2)
C(19)	0.4056 (3)	0.6779 (3)	-0.0654 (3)	5.5 (2)
C(20)	0.4442 (3)	0.7305 (2)	0.0197 (3)	5.3 (2)
C(21)	0.4491 (3)	0.6981 (2)	0.1220 (2)	4.5 (1)
C(22)	0.3049 (3)	0.4294 (2)	0.4455 (2)	4.7 (1)

[a] B_{eq} is defined as one-third of the trace of the orthogonalized B_{ij} tensor.

EXPERIMENTAL

Melting points were determined on a Büchi 510 apparatus and are uncorrected. The uv spectra were recorded on a Perkin Elmer Lambda 5 spectrophotometer using 1 cm quartz cells in a 10⁻⁵ M ethanol solution. The wavelength absorption maxima are reported in nanometers.

The ¹H nmr spectra were recorded with a Bruker AMX-400 WB (Centro Interdipartimentale Grandi Strumenti, Modena University) operating at 400.13 MHz. Chemical shifts are reported in ppm from tetramethylsilane used as internal standard, and are given in δ units. Microanalyses were carried out by R. Gallesi in the Microanalysis Laboratory of the Dipartimento di Scienze Farmaceutiche, Modena University. The compounds were separated by a Büchi model 685 (mpc) glass column (460 x 36 mm I.D.), dry-filled with silica gel 60 (particle size 0.015-0.040 mm) (Merck) and connected to an LKB Multirac 2111 fraction collector. The fractions were monitored using 5 x 10 cm tlc plates (Merck).

High Performance Thin Layer Chromatography (hptlc).

Samples were applied to the plates by means of a Linomat IV (Camag) spotter on 10 x 20 cm hptlc plates (Merck). All the

plates were developed at room temperature using the ascending mode. For the separation of **2** from **3** and **4**, and **6** from **7** the solvent system used was toluene/ethyl acetate (1:1, v/v). The starting products **1** and **5** were determined using toluene/ethyl acetate/ethanol (4:4:1, v/v/v) for the second run. The layers were analysed at 254 nm by the fluorescence-quenching method using a Camag TLC Scanner II equipped with an Olivetti M280 PC operating the "Cats 3.04" scanning program. The scanner was set up as follows: band width, 10 nm; span, 25; slit, 5 x 0.2 mm; scanning speed, 5 mm/sec. The calibration graphs were plotted for each plate using the linear regression equation obtained from the area values under the peaks for different amounts of standard solution. The linearity correlation coefficient was between 0.9985 and 0.9998 for all compounds.

Crystallography.

Prismatic colourless crystals, suitable for X-ray analysis, were in both cases grown from acetone/petroleum ether (bp 60-80°) solution. All X-ray measurements were carried out on Enraf-Nonius CAD4 diffractometer, at room temperature, under the conditions reported in Table 3. Data reduction included Lp and absorption (based on empirical ψ scan) corrections.

Both structures were solved by direct methods (SHELX-86 program [19]), and were refined through full-matrix least-squares calculations using the SHELX-76 program [20]. In both cases, all non-hydrogen atoms were refined anisotropically, whereas the hydrogen atoms, located in ΔF maps, were refined isotropically (with common temperature factors) through the some least-squares cycles and then kept fixed owing to the low parameter/reflection ratios. Complex neutral-atom scattering factors were taken from the literature [21]. Major calculations were carried out on a Digital Alpha 6000/800 computer. Final fractional coordinates and equivalent isotropic temperature factors for non-hydrogen atoms are given in Tables 4 and 5. Selected bond distances, bond and torsion angles are reported in Table 4. Lists of anisotropic temperature factors, positional and thermal parameters for hydrogen atoms, complete bond distances and bond angles, shortest van der Waals contacts, torsion angles, selected least-squares planes and observed and calculated structure factors are available on request from the authors.

1-Benzenesulfonyl-1*H*-benzimidazol-2-ylamine (**2**) and *N*-(1-Benzene-sulfonyl-1,3-dihydrobenzimidazol-2-ylidene)-benzenesulfonamide (**4**).

Compound **1** (0.5 g, 3.75 mmoles) was dissolved in 3 ml of anhydrous pyridine to which 1 equivalent of benzenesulfonyl chloride was added with constant stirring for one hour at 50°. The residue obtained after the addition of water was a mixture of **2** and **4**. These compounds were separated by mpc with the mobile phase toluene/ethyl acetate (1:1, v/v) to give compounds **2** and **4**.

Compound **2** was obtained in 35% yield (0.36 g), mp 194° (acetone/water); ir (nujol): 3300-3255, 1369-1180 cm⁻¹; uv (ethanol): λ_{max} 244 nm (log ε 3.23); ¹H nmr (DMSO-d₆): δ 7.29 (s, 2H, NH₂).

Anal. Calcd. for C₁₃H₁₁N₃O₂S: C, 57.13; H, 4.06; N, 15.38. Found: C, 57.18; H, 4.10; N, 15.21.

Compound **4** was obtained in 38% yield (0.59 g), mp 242-243° (acetone/petroleum ether (bp 60-80°)); ir (nujol): 3257, 1301-1175, 1278-1145 cm⁻¹; uv (ethanol): λ_{max} 288.1 nm (log ε 3.15), λ_{max} 251.6 nm (log ε 3.23); ¹H nmr (DMSO-d₆): δ 12.40

(s, 1H, NH).

Anal. Calcd. for $C_{19}H_{15}N_3O_4S_2$: C, 55.19; H, 3.66; N, 10.16. Found: C, 54.98; H, 3.72; N, 10.14.

N-(1,3-Dihydrobenzoimidazol-2-ylidene)benzenesulfonamide (3).

Compound 1 (0.5 g, 3.75 mmoles) was dissolved in 3 ml of anhydrous pyridine to which 1 equivalent of benzenesulfonyl chloride was added with constant stirring for one week at 50°. The residue obtained after the addition of water was a mixture of 3 and 4. The solid obtained was treated with 4*N* sodium hydroxide. The insoluble part was 4, while the alkaline solution, after precipitation with acetic acid, gave 0.41 g (40%) of 3, mp >300° (acetone/water) (lit 356° [22]); ir (nujol): 3371, 1291-1140 cm^{-1} ; uv (ethanol): λ_{max} 288.6 nm (log ϵ 3.31); 1H nmr (DMSO- d_6): δ 12.10 (s, 2H, NH).

Anal. Calcd. for $C_{13}H_{11}N_3O_2S$: C, 57.13; H, 4.06; N, 15.38. Found: C, 57.20; H, 4.05; N, 15.08.

1-Methyl-1*H*-benzoimidazol-2-ylamine (5).

Compound 5 was prepared according to the literature [23], mp 193-194° (toluene) (lit 202-204° [23]); ir (nujol): 3447-3302; uv (ethanol): λ_{max} 283.9 nm (log ϵ 2.98), λ_{max} 246.5 nm (log ϵ 2.79); 1H nmr (DMSO- d_6): δ 6.41 (s, 2H, NH₂), 3.58 (s, 3H, CH₃).

Anal. Calcd. for $C_8H_9N_3$: C, 65.29; H, 6.16; N, 28.55. Found: C, 65.31; H, 6.16; N, 28.66.

N-(1-Methyl-1,3-dihydrobenzoimidazol-2-ylidene)benzenesulfonamide (6) and *N*-(1-Benzenesulfonyl-3-methyl-1,3-dihydrobenzoimidazol-2-ylidene)benzenesulfonamide (7).

Compound 5 (0.5 g, 3.40 mmoles) was dissolved in 3 ml of anhydrous pyridine to which 2 equivalents of benzenesulfonyl chloride was added with constant stirring for one day at 50°. The precipitate obtained after the addition of water was a mixture of 6 and 7. The mixture was treated with 4*N* sodium hydroxide. The insoluble part was compound 7. The alkaline solution was acidified with acetic acid to precipitate 6.

Compound 6 was obtained in 32% yield (0.31 g), mp 221-222° (acetone/petroleum ether (bp 60-80°)); ir (nujol): 3297, 1277-1210 cm^{-1} ; uv (ethanol): λ_{max} 290 nm (log ϵ 2.33); 1H nmr (DMSO- d_6): δ 11.95 (s, 1H, NH), 3.55 (s, 3H, CH₃)

Anal. Calcd. for $C_{14}H_{13}N_3O_2S$: C, 58.52; H, 4.56; N, 14.62. Found: C, 58.55; H, 4.70; N, 14.68.

Compound 7 was obtained in 39% yield (0.57 g), mp 242-243° (acetone/petroleum ether (bp 60-80°)); ir (nujol): 1284-1085 cm^{-1} ; uv (ethanol): λ_{max} 289.5 nm (log ϵ 2.72); 1H nmr

(DMSO- d_6): δ 3.94 (s, 3H, CH₃).

Anal. Calcd. for $C_{20}H_{17}N_3O_4S_2$: C, 56.20; H, 4.01; N, 9.84. Found: C, 56.48; H, 4.14; N, 9.59.

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