MOLECULAR STRUCTURE OF 1-MORPHOLINO-3-PHENYL-5,6,7,8-TETRACHLORO-1,2,4-BENZOTHIADIAZINE

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We recently reported [1] the synthesis and molecular structure of 1,5,6,7,8-pentachloro-3-phenyl-1,2,4-benzothiadiazine (I), which is a highly reactive compound that can serve as the starting compound in syntheses of a whole series of substituted benzothiadiazines of a new type owing to the presence of a mobile chlorine atom at the sulfur atom.* The molecule of compound I is characterized by a planar configuration for the heterocycle [1, 2]. Continuing our study of the structural features of 1,2,4-benzothiadiazine systems, we carried out an x-ray structural investigation of 1-morpholino-3-phenyl-5,6,7,8-tetrachloro-1,2,4-benzothiadiazine (II) for the purpose of determining whether the planar configuration of the heterocycle in I is a common property of such 1,2,4-benzothiadiazine systems or whether the planarity depends on the nature of the exocyclic substituent at the sulfur atom of the heterocycle.

The unit-cell parameters and the intensities of 1151 independent reflections with $I > 3\sigma$ (II) were measured on an RÉD-4 four-circle diffractometer (Mo $K\alpha$ radiation, ω scanning at the rate of 8 deg/min, $\sin\theta/\lambda \leqslant 0.6$ Å^{-1}). The crystals of II are monoclinic: $a = 13.445(5)$, $b = 8.269(5)$, $c = 17.096(5)$ Å, $\gamma = 73.53(3)°$, $V = 1822.7$ Å^3, $Z = 4$, $d_{cal} = 1.64$ g/cm^3, space group $P2_1/b$. The structure was interpreted with the aid of the MULTAN program [3] and refined in the anisotropic approximation in the framework of the XTLSM system of programs [4]. The H atoms were located in a difference synthesis of the electron density and refined in the isotropic approximation. The final values of the residuals were $R = 0.061$ and $R_w = 0.055$. The coordinates of the basis atoms are presented in Table 1, and the overall form of molecule II and its principal geometric parameters are presented in Fig. 1.

*A suspension of 0.004 mole of compound I in 30 ml of benzene is given a dropwise addition of a solution of 0.008 mole of morpholine in 5 ml of benzene with stirring at 15-20°C. The mixture is stirred for 1.5 h at 50°C and cooled to 20°C, and the hydrochloride salt of morpholine is filtered out. The filtrate is evaporated in a vacuum (10-20 mm Hg). 1-Morpholino-3-phenyl-5,6,7,8-tetrachloro-1,2,4-benzothiadiazine (II) remains in the beaker. The product is then purified by crystallization from a 3:2 acetonitrile—DMFA mixture. The yield was 56%, and mp = 190°C.

TABLE 1. Coordinates of Basis Atoms* ($\times 10^4$)

Atom	x/a	y/b	z/c	Atom	x/a	y/b	z/c
S	6477(2)	3524(4)	125(2)	C(5)	8981(9)	1823(14)	—1228(7)
Cl(1)	7332(3)	—247(4)	642(2)	C(6)	8102(8)	2908(14)	—875(7)
Cl(2)	9294(3)	—2633(4)	—191(2)	C(7)	6885(8)	5523(14)	—897(6)
Cl(3)	10471(3)	—1070(5)	—1429(2)	C(8)	6584(9)	7297(13)	—1183(7)
Cl(4)	9602(3)	2603(5)	—1956(2)	C(9)	7258(9)	7841(14)	—1681(7)
N(1)	7795(7)	4564(11)	—1098(5)	C(10)	6993(9)	9490(15)	—1967(7)
N(2)	6138(7)	5102(11)	—460(5)	C(11)	6069(10)	10614(16)	—1727(7)
N(3)	6965(7)	4087(11)	950(5)	C(12)	5424(10)	10115(16)	—1217(8)
O	7222(7)	6311(11)	2148(5)	C(13)	5668(9)	8452(15)	—955(7)
C(1)	7628(8)	2221(13)	—296(6)	C(14)	7709(9)	5089(15)	861(7)
C(2)	7981(8)	513(14)	—84(7)	C(15)	8067(10)	5497(16)	1681(8)
C(3)	8830(9)	—529(14)	—441(7)	C(16)	6558(10)	5315(17)	2269(8)
C(4)	9327(9)	140(14)	—1013(7)	C(17)	6110(10)	4927(16)	1500(8)

*The coordinates of the H atoms can be obtained from the authors.

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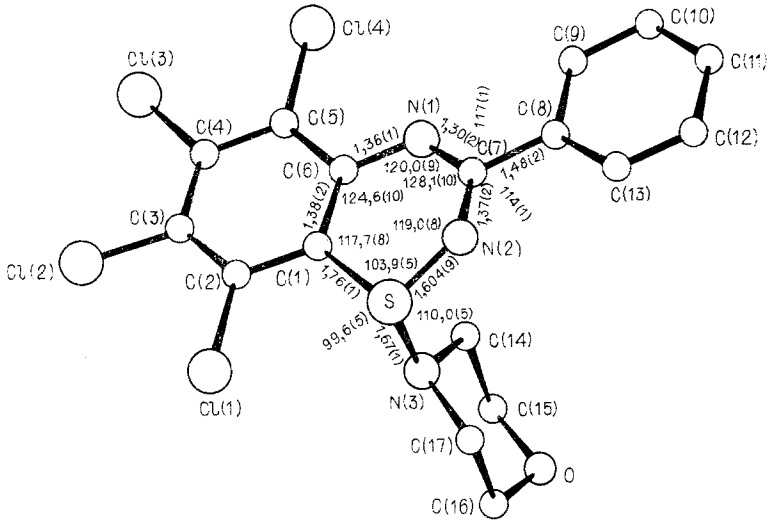

Fig. 1. Overall form of molecule II and its principal geometric parameters.

It was established as a result of an x-ray structural investigation that the planarity of the 3-phenyl-1,2,4-benzothiadiazine system is markedly dependent on the exocyclic substituent at the carbon atom. In fact, when the chlorine atom in compound I is replaced by the bulkier substituent in molecule II, the dihedral angles between the sulfur-containing SN(2)C(7)N(1)C(6)C(1) heterocycle and the C(1)...C(6) and C(8)...C(13) benzene rings increase from 5.1 and 5.4° in I to 9.9 and 7.1° in II, and the dihedral angle between the benzene rings increases from 2.9 to 8.6°. At the same time, the deviation of the thiadiazine heterocycle from planarity increases significantly. For example, while this ring is planar in I to within 0.08(1) Å, the deviations of the atoms from the mean-square plane in II reach 0.17(1) Å, and its conformation is distorted in the direction of a strongly flattened "half-chair" (the modified Cremer–Pople parameters [5] are: $S = 0.01$, $\theta = 41.5°$, $\psi_2 = 189.1°$). The sulfur atoms in I and II have pyramidal bond configurations (the sums of the bond are equal to 313.1 and 313.5°). The bond lengths in the thiadiazine rings in compounds I and II coincide to within 5σ. The exocyclic S–N(3) bond in II has a length equal to 1.67(1) Å, which falls in the usual range for S^{III}–N(sp^3) single bonds* [6]. At the same time, the formally double endocyclic S=N(2) bond with a length equal to 1.604(9) Å is appreciably elongated in comparison to the values of 1.45 Å for an S^{III}=N bond [7] and 1.53 Å for an S^{II}=N [8], while the formally single S–C(1) bond with a length equal to 1.76(1) Å is shortened in comparison to the value of 1.80 Å for an S^{III}–C(sp^2) single bond [9]. The bond lengths N(1)–C(7) = 1.30(2), N(1)–C(6) = 136(1), and N(2)–C(7) = 1.37(2) Å are close to the value of 1.34 Å corresponding to a C(sp^2)–N(sp^2) bond with an order equal to 1.5 [10]. The geometric parameters of the morpholine ring in II fall within the usual ranges [11].

LITERATURE CITED

1. Yu. G. Shermolovich, Yu. A. Simonov, A. A. Dvorkin, et al., Zh. Org. Khim., **25**, No. 3, 612-615 (1989).
2. L. N. Markovskii, V. S. Talanov, O. M. Polumbrik, et al., Zh. Org. Khim., **17**, 2619-2620 (1981).
3. P. Main, S. J. Fiske, S. E. Hull, et al., MULTAN-80. A System of Computer Programs for Automatic Solution of Crystal Structures from X-Ray Diffraction Data, University of York, England and Louvain, Belgium (1980).
4. V. K. Pecharskii, P. O. Zavalii, L. G. Aksel'rud, et al., Vestn. L'vovsk. Univ., Ser. Khim., 9-12 (1984).
5. N. S. Zefirov and V. A. Palyulin, Dokl. Akad. Nauk SSSR, **252**, 111-115 (1980).
6. W. Feder, H. Drisler, H. D. Rudolah, et al., Naturforsch., **24A**, 266-270 (1969).
7. R. R. Karl, S. H. Baner, Inorg. Chem., **14**, 1859-1861 (1975).
8. B. Beagley, S. J. Chatrell, R. G. Kirby, and D. G. Schmilling, J. Mol. Struct., **25**, 319-327 (1975).
9. B. Rozsandai, J. H. Moore, D. C. Gregory, and J. Hargittai, J. Mol. Struct., **51**, 69-76 (1979).
10. M. Burke-Laing and M. Laing, Acta Crystallogr., **B32**, 3216-3224 (1976).
11. S. C. Nyburg and F. H. Pickard, Cryst. Mol. Struct., **3**, 343-348.

*Here and in the following the superscripted Roman numeral indicates the coordination number of sulfur.