Molecular and crystal structure of 4,5,4′,5′-tetrahydro-2,2′-(1,4-phenylene)bisoxazoline

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4,5,4′,5′-Tetrahydro-2,2′-(1,4-phenylene)bisoxazoline, which is one of the most promising stabilizers-consolidators of heterochain polymers, was studied by X-ray structural analysis.

Key words: 4,5,4′,5′-tetrahydro-2,2′-(1,4-phenylene)bisoxazoline, heterochain polymers; X-ray structural study.

4,5,4′,5′-Tetrahydro-2,2′-(1,4-phenylene)bisoxazoline (**1**) is one of the most promising stabilizers-consolidators of heterochain polymers.[1–4] The stabilizing capability of compound **1** is based on its reaction with the terminal functional groups of these polymers (for example, with the hydroxyl and carbonyl groups of polyesters, with the amino groups of polyamides, *etc.*). The products obtained are less sensitive to high temperature and moisture on processing. With the aim of establishing the structural-chemical characteristics, which could affect the reactivities of related reagents in cycloaddition, compound **1** was studied by X-ray structural analysis.[5]

†Deceased.

Table 1. Coordinates ($\times 10^4$) and isotropic (equivalent isotropic for nonhydrogen atoms) thermal parameters ($\times 10^3$) of the atoms in the structure of **1**

Atom	*x*	*y*	*z*	U/Å^2
C(1)	1037(3)	8921(2)	6018(2)	14(1)
C(2)	−413(3)	10171(2)	6827(2)	16(1)
C(6)	1453(3)	8756(2)	4182(2)	16(1)
N(1′)	1850(3)	7787(2)	8756(2)	21(1)
C(2′)	2139(3)	7782(2)	7104(2)	14(1)
O(3′)	3598(2)	6675(2)	6234(2)	23(1)
C(4′)	4572(4)	5793(3)	7591(2)	20(1)
C(5′)	3338(3)	6498(3)	9282(2)	18(1)
H(2)	−708(33)	10292(29)	8050(27)	24(5)
H(6)	2431(34)	7878(30)	3607(26)	22(4)
H(4′a)	4003(32)	4167(30)	6896(24)	17(4)
H(4′b)	6420(40)	6633(32)	8018(26)	28(5)
H(5′a)	2170(32)	5194(28)	9412(23)	15(4)
H(5′b)	4652(35)	7512(31)	10566(27)	27(5)

The geometric parameters of compound **1** are given in Tables 1 and 2. It was found that in the crystal, molecule **1** (Fig. 1) is located on an inversion center. The molecule is nearly planar (the maximum deviation of the atoms, including the H(2), H(3), H(5), and H(6) atoms, from the mean plane is no more than 0.021 Å). Apparently, flattening of the molecule is favored by the presence of a long chain of conjugated bonds (see Table 2).

The structural parameters of compound **1**, which were determined by an X-ray structural study, suggest that because of the absence of noticeable steric hindrances and the accessibility of the C(2′) and C(2′a) atoms for nucleophilic attack by such groups as —OH and $-NH_2$, compound **1** can be involved in chemical transformations of macromolecules containing the above-

Table 2. Bond lengths (*d*) and bond angles (ω) in the structure of **1**

Bond	*d*/Å	Angle	ω/deg
N(1′)—C(2′)	1.271(2)	C(2′)—C(1)—C(2)	119.8(1)
N(1′)—C(5′)	1.474(3)	C(2′)—C(1)—C(6)	120.4(2)
C(2′)—O(3′)	1.356(2)	C(2)—C(1)—C(6)	119.8(2)
C(2′)—C(1)	1.479(3)	C(1)—C(2)—C(3)	120.2(2)
O(3′)—C(4′)	1.459(3)	C(1)—C(6)—C(5)	120.0(2)
C(4′)—C(5′)	1.536(3)	C(2′)—N(1′)—C(5′)	106.4(2)
C(1)—C(2)	1.393(3)	N(1′)—C(2′)—O(3′)	118.8(2)
C(1)—C(6)	1.403(2)	N(1′)—C(2′)—C(1)	125.6(2)
C(2)—C(3)	1.387(3)	O(3′)—C(2′)—C(1)	115.6(1)
		C(2′)—O(3′)—C(4′)	106.1(1)
		O(3′)—C(4′)—C(5′)	103.4(2)
		N(1′)—C(5′)—C(4′)	105.2(1)

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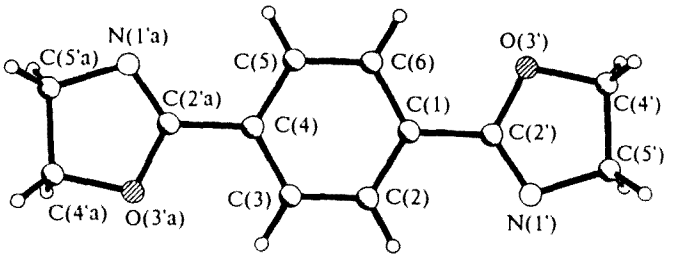

Fig. 1. Structure of molecule **1**.

mentioned groups in the course of processing of polymers.

Experimental

4,5,4′,5′-Tetrahydro-2,2′-(1,4-phenylene)bisoxazoline was synthesized from dimethyl terephthalate and monoethanolamine followed by cyclization of bis-*N*-(2-oxyethyl)amide of terephthalic acid that formed. Bisoxazoline **1** is a white crystalline compound, m.p. 241.0—241.5 °C. The IR spectrum shows an absorption band of the —C=N stretching vibration ν(C=N) = 1645 cm^{-1}. In the ^1H NMR spectrum of 4,5,4′,5′-tetrahydro-2,2′-(1,4-phenylene)bisoxazoline in $CDCl_3$, the signals are partially overlapping multiplets ($J_{45} \cong 7$—8 Hz); the chemical shifts are as follows: 4 H — 4.20 ppm and 5 H — 4.31 ppm.[6—7]

The crystals of compound **1** are triclinic, at −120 °C: a = 5.674(2) Å, b = 6.646(2) Å, c = 7.503(2) Å, α = 109.72(1)°, β = 97.91(1)°, γ = 107.39(1)°, V = 244.9(1) $Å^3$, Z = 1 (the molecule occupies a special position, namely, an inversion center), d_{calc} = 1.466 g cm^{-3}, space group $P\bar{1}$, $C_{12}H_{12}N_2O_2$, M = 216.2. The unit cell parameters and intensities of 1255 reflections were measured on an automated four-circle Siemens P3/PC diffractometer (153 K, λ(Mo-Kα) radiation, graphite monochromator, θ/2θ scanning technique, θ_{max} = 27°). The structure was solved by the direct method and refined by the full-matrix least-squares method with anisotropic thermal parameters for nonhydrogen atoms. The hydrogen atoms were located from the difference Fourier synthesis and refined isotropically. The atomic coordinates and isotropic thermal parameters (equivalent isotropic thermal parameters for nonhydrogen atoms) are given in Table 1. The final values of the R factors were as follows: R = 0.035 and R_w = 0.035 using 741 independent reflections with $I > 3\sigma(I)$. All calculations were carried out on an IBM PC/AT-386 computer using the SHELXTL PLUS program package.[8]

References

1. L. Buxbaum, F. Breitenfoellner, and T. Kammueller, Eur. Pat. 74337; *Chem. Abstrs.*, 1983, **99**, 6538x.
2. Jap. Pat 80161823; *Chem. Abstrs.*, 1981, **94**, 193102g.
3. Jap. Pat. 80164218; *Chem. Abstrs.*, 1981, **94**, 193100e.
4. Jap. Pat. 62257930; *Chem. Abstrs.*, 1988, **108**, 133316b.
5. A. J. Frump, *Chem. Rev.*, 1971, 483.
6. H. Witte and W. Seeliger, *Angew. Chem.*, 1972, 343.
7. L. I. Belen′kii, M. A. Cheskis, V. P. Zvolinskii, and A. E. Obukhov, *Khim. Geterotsikl. Soedin.*, 1986, 826 [*Chem. Heterocycl. Compd.*, 1986 (Engl. Transl.)].
8. W. Robinson and G. M. Sheldrick, SHELX in *Crystallographic Computing Techniques and New Technologies*, Eds. N. W. Isaaks and M. R. Taylor, Oxford Univer. Press, Oxford, 1988, 366.

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