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# SPATIAL STRUCTURE OF 2-BENZOYL-3-METHOXY-5-METHYLISOXAZOLIDINE

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The nuclear Overhauser effect and x-ray diffraction analysis have been employed to determine the spatial structure of the diastereoisomeric 2-benzoyl-3-methoxy-5-methyl-isoxazolidines. It has been found that the predominant isomer in the reaction mixture has the cis-configuration.

We have previously shown that substituted hydroxamic acids react with crotonaldehyde to give a mixture of the two diastereoisomeric pairs of 3-hydroxyisoxazolidines, in a ratio of 1:1 [1], although in solution this ratio may vary, since these compounds undergo ring-chain tautomerism. In order to exclude the influence of this factor and also of intermolecular hydrogen bonding, the stereochemistry of the functionally substituted isoxazolidines obtained was examined in the case of 2-benzoyl-3-methoxy-5-methylisoxazolidine, obtained as in [2]. This compound consists of a mixture of the diastereoisomeric pairs (I) and (II) in a ratio of 2:1, this ratio being constant under the reaction conditions, probably as a result of the differing stabilities of the isomers.
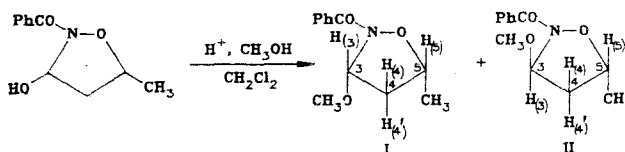


Quantitative separation of the mixture into its diastereoisomers was carried out by high performance flash chromatography (see Experimental), to give enriched mixtures with (I):(II) ratios of 20:1 and 1:6. For the spectral studies, mixtures with (I):(II) 20:1 and 1:1 were used.

To determine the configurations of the diastereoisomers (I) and (II), we measured the stationary proton-proton nuclear Overhauser effect (NOE) by difference spectroscopy [3]. The NOE was expressed as a percentage from the expression:

$$\eta_i(s) = \frac{I - I_0}{I_0} \cdot 100,$$

where $I_0$ is the integral intensity of the signal for proton i in the normal spectrum, and I the intensity when the nucleus s is saturated. Comparison of the internuclear distances in the molecule from the NOE was carried out only for protons with approximately the same spin-lattice relaxation times. The NOE experiments with (I) and (II) were carried out under the same conditions (temperature, concentration, solvent, etc.). The spin-lattice relaxation times and the NOE for (I) and (II) are given in Table 1.

On saturation of the signal for the 4'-H in isomer (I), the NOE was observed only for the geminal 4-H proton, and irradiation fo the 4-H signal gave rise to a considerable NOE for atoms 3-H and 5-H (13.8 and 11.6%, respectively). Saturation of the 3-H and 5-H signals resulted in an increase in the intensity of the signal for the 4-H proton (5.8 and 5.7%), while no NOE was observed for the 4'-H atom. On the other hand, saturation of the signal for the methyl group gave rise to a small NOE for the 4'-H proton. Consequently, atoms 3-H and 5-H are located cis- to 4-H, and trans- to 4'-H. This leads to the conclusion that the isoxazolidine (I) is the cis-isomer.

Irradiation of the 4-H proton in the diastereoisomer (II) results in an increase in intensity of the signal for 5-H (12.4%), but gives rise to no NOE for 3-H. On saturation of the signal for 4'-H, the NOE was seen only for 3-H (12.5%). Saturation of the 3-H signal causes an increase in the intensity of the signal for 4'-H, and saturation of 5-H gives rise to an NOE for 4-H (4.7%). It follows that protons 3-H and 4'-H, like 5-H and 4-H, are located in the cis-position, and the isoxazolidine (II) is the trans-isomer.

We also carried out an independent x-ray diffraction examination of the isomer (I). A general view of the molecule is shown in Fig. 1, the bond lengths being given in Table 2, and the valence angles in Table 3. In all the previously studied isoxazolidines which do not contain polycyclic fragments, the heterocycle has the envelope conformation. In most cases, the nitrogen stands out from the plane of the other four ring atoms [4-7]. Also known are the $C_{(3)}$- [8] and $C_{(5)}$-envelope [9] conformations. In contrast to the previously examined isoxazolidines, in (I) the heterocycle has the $O_{(1)}$-envelope conformation, the $O_{(1)}$ atom standing out from the plane (to within 0.030(3) Å) $NC_{(3)}C_{(4)}C_{(5)}$ by 0.350(2) Å. The bending angle of the ring along the $N-C_{(5)}$ axis is 38.5°. Despite its unusual conformation, the other geometric parameters for the isoxazolidine ring, and for the molecule as a whole, have the usual values. The methyl and methoxy groups are located on the same side of the mean square plane of the heterocycle, the former occupying a pseudoequatorial position. The valence configuration of the nitrogen in (I) is more planar than in previously reported isoxazolidines [4-9], the sum of the valence angles at N being 344.1°, and its departure from the plane $O_{(1)}C_{(3)}$-$C_{(6)}$ 0.320(2) Å. The plane of the carbonyl group $O_{(3)}NC_{(6)}C_{(7)}$ forms a dihedral angle of 55.2° with the mean square plane of the heterocycle, and an angle of 38.5° with the plane of the benzene ring. In the crystal, the molecules of (I) are bonded together by van der Waals interactions only, there being no shortened intermolecular contacts.

The x-ray diffraction results, as well as the NMR spectroscopic findings, therefore show that the isomer (I), which predominates in the reaction mixture, has the cis-configuration. The stereochemistry of molecules containing few heteroatoms (in the present case, four) is largely determined by stereoelectronic factors, manifested in the case of cyclic compounds as the general anomeric effect, the exo-anomeric effect, and the gauche-effect [10]. The predominance of the cis-configuration in 2-benzoyl-3-methyl-5-methylisoxazolidine suggests that the cis-isomer is more thermodynamically stable, and is governed by the sum of stereoelectronic factors, namely the anomeric effect due to interaction of the lone pairs of the ring nitrogen and the exocyclic oxygen, the exo-anomeric effect as a result of which the $OCH_3$ group is situated relative to the ring in such a way that the substituents are gauche to the $C_{(3)}-O_{(2)}$ bond, and the gauche-effect, which confers considerable stabilization by virtue of the gauche orientation of the lone pairs of the adjacent heteroatoms (N and O in the ring). Fairly stable, unscreened configurations could thus be formed by both the cis- and trans-isomers, but in the case of the cis-isomer the relative positions of the lone pairs of the heteroatoms in the most favored conformer from the point of view of anomeric effects is more favored than in the trans-isomer. (Formula, top, page following Table 1 and Figs. 1 and 2.)

It may be assumed that it is this factor which confers greater thermodynamic stability on the cis- than on the trans-isomer.

TABLE 1. Spin-Lattice Relaxation Times ($T_1$, sec) and NOE Values ($\eta$) for Protons in (I) and (II)

| $T_1$ | Observed protons | $\eta$, %, on irradiation of protons | | | | |
|---|---|---|---|---|---|---|
| | | 3-H* | 5-H | 4-H | 4'-H | CH₃ |
| Isomer (I) | | | | | | |
| 3,94 | 3-H | — | 1,2 | 13,8 | — | — |
| 3,54 | 5-H | 1,1 | — | 11,6 | — | 15,0 |
| 1,41 | 4-H | 5,8 | 5,7 | — | 27,2 | — |
| 1,63 | 4'-H | — | — | 27,3 | — | 3,80 |
| 1,40 | CH₃ | — | 1,9 | — | 1,1 | — |
| Isomer (II) | | | | | | |
| 3,85 | 3-H | — | 0,2 | 1,9 | 12,5 | 0,7 |
| 5,33 | 5-H | 0,7 | — | 12,4 | 0,9 | 13,7 |
| 1,82 | 4-H | 0,7 | 4,7 | — | 26,7 | — |
| 1,62 | 4'-H | 4,6 | 0,3 | 28,5 | — | 5,90 |
| 1,55 | CH₃ | — | 1,5 | — | — | — |

*On saturation of the 3-H proton, NOE was seen for the OCH₃ group (~3%).
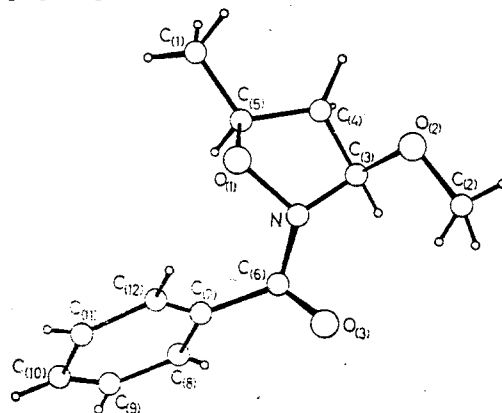


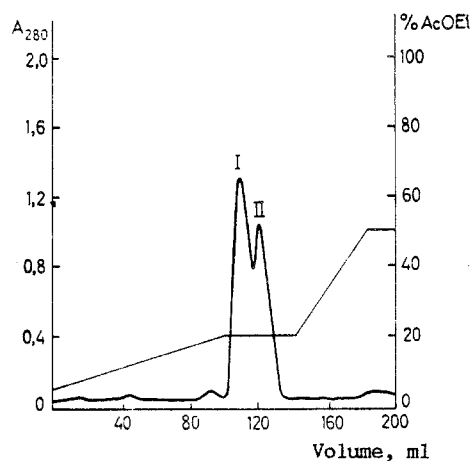Fig. 1. General view of the molecule of (I).



Fig. 2. Chromatogram of a mixture of diastereoisomers of 2-benzoyl-3-methoxy-5-methylisoxazolidine on a 16 × 100 mm column of Silpearl, in the system hexane—ethyl acetate. Sample volume 25 μl, saturated solution in chloroform. Elution rate 4 ml/min. Gradient: amount of ethyl acetate from 5 to 20% in 100 ml, 20% in 40 ml, from 20 to 50% in 40 ml, and 50% in 20 ml.

cis-isomer·                    trans-isomer
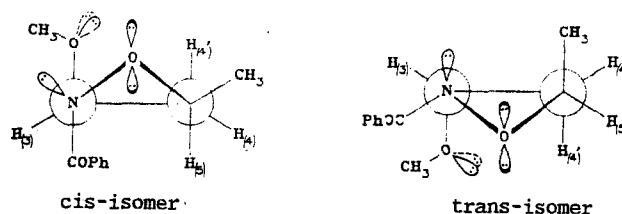
## EXPERIMENTAL

The purity and extent of separation of the compounds were checked by TLC on Silufol UV-254 plates in the system hexane-ethyl acetate, 3:1 (Fig. 2). Optimization of the conditions for the chromatographic resolution of the diastereoisomers was carried out on a Pharmacia FPL C medium pressure liquid chromatograph with a 16 × 100 mm column with Silpearl, detection by absorption at $\lambda$ 280 nm ($\varepsilon_{280}$ 9.2·$10^3$). The basic system used was hexane-ethyl acetate. Quantitative resolution was achieved using flash-chromatography on a 20 × 200 mm column with Silpearl, and gradient elution from ethyl acetate to hexane (Fig. 2). The enriched mixtures obtained were: a) (I):(II) = 20:1, mp 56°C, $R_f$ 0.47; and b) (I):(II) = 1:6, oil, $R_f$ 0.43. The UV spectrum was recorded on a Specord UV-vis in dichloromethane.

PMR spectra were obtained on a Varian XL-400 spectrometer in $CDCl_3$ at 27°C, internal standard TMS. For the spectral studies, mixtures of (I):(II) of 20:1 and 1:1 were used. The samples were first degassed, then sealed in vacuo.

Assignment of the signals was carried out from $^1H-\{^1H\}$ double resonance experiments. The proton chemical shifts and the H-H coupling constants are given in Table 4. Spin-lattice relaxation times were measured by the inversion-reduction method. The errors in the measurement of $T_1$ did not exceed 5%. The NOEDIF program was used for the NOE experiments [11]. Two spectra were accumulated alternately, namely 1) 16 runs at a decoupler frequency set at the frequency of the proton to be saturated, and 2) 16 runs with the decoupler frequency set at off-resonance. The total numbers of runs for each spectrum were 128 and 256. When the experiment was complete, spectrum (2) was subtracted from spectrum (1). The difference spectrum gave the value of the NOE. The signals were saturated by successive selective irradiation with four frequencies in a saturating multiplet. The saturation times at each frequency were chosen from the proton relaxation time, and the ring was recycled repeatedly during the saturation period, which was 20 sec for the cis-isomer and 25 sec for the trans-isomer. A 90° impulse was used for the observation.

cis-2-Benzoyl-3-methoxy-5-methylisoxazolidine (I). Monoclinic crystals. At 20°C, a = 9.168(1), b = 15.473(1), c = 9.097(1), Å; $\beta$ = 113.14(1)°; Z = 4, space group P2₁/c. The cell parameters and the intensities of 1679 reflections, 1501 of which with I $\geq$ 2σ were used for calculation and refinement of the structure, were measured on a Hilger-Watts diffractometer

TABLE 2. Bond Lengths d in (I)

| Bond | $d$, Å | Bond | $d$, Å | Bond | $d$, Å |
|---|---|---|---|---|---|
| $C_{(1)}-C_{(5)}$ | 1,500(4) | $C_{(3)}-O_{(2)}$ | 1,406(3) | $C_{(8)}-C_{(9)}$ | 1,379(3) |
| $C_{(5)}-O_{(1)}$ | 1,453(3) | $O_{(2)}-C_{(2)}$ | 1,423(3) | $C_{(9)}-C_{(10)}$ | 1,365(4) |
| $O_{(1)}-N$ | 1,416(2) | $N-C_{(6)}$ | 1,380(3) | $C_{(10)}-C_{(11)}$ | 1,372(4) |
| $N-C_{(3)}$ | 1,475(3) | $C_{(6)}-O_{(3)}$ | 1,215(3) | $C_{(11)}-C_{(12)}$ | 1,390(3) |
| $C_{(3)}-C_{(4)}$ | 1,523(3) | $C_{(6)}-C_{(7)}$ | 1,493(3) | $C_{(12)}-C_{(7)}$ | 1,374(3) |
| $C_{(4)}-C_{(5)}$ | 1,511(3) | $C_{(7)}-C_{(8)}$ | 1,392(3) | | |

TABLE 3. Valence Angles ω (deg) in (I)

| Angle | ω | Angle | ω | Angle | ω |
|---|---|---|---|---|---|
| $NO_{(1)}C_{(5)}$ | 104,2(2) | $C_{(3)}C_{(4)}C_{(5)}$ | 105,0(2) | $C_{(6)}C_{(7)}C_{(12)}$ | 123,8(2) |
| $C_{(2)}O_{(2)}C_{(3)}$ | 113,8(2) | $O_{(1)}C_{(5)}C_{(1)}$ | 108,2(2) | $C_{(12)}C_{(7)}C_{(8)}$ | 119,7(2) |
| $O_{(1)}NC_{(3)}$ | 108,0(2) | $O_{(1)}C_{(5)}C_{(4)}$ | 103,3(2) | $C_{(7)}C_{(8)}C_{(9)}$ | 120,0(2) |
| $O_{(1)}NC_{(6)}$ | 117,3(2) | $C_{(1)}C_{(5)}C_{(4)}$ | 116,6(2) | $C_{(8)}C_{(9)}C_{(10)}$ | 120,2(2) |
| $C_{(3)}NC_{(6)}$ | 119,8(2) | $O_{(3)}C_{(6)}N$ | 119,7(2) | $C_{(9)}C_{(10)}C_{(11)}$ | 120,1(2) |
| $O_{(2)}C_{(3)}N$ | 111,6(2) | $O_{(3)}C_{(6)}C_{(7)}$ | 121,7(2) | $C_{(10)}C_{(11)}C_{(12)}$ | 120,5(2) |
| $O_{(2)}C_{(3)}C_{(4)}$ | 108,2(2) | $NC_{(6)}C_{(7)}$ | 118,5(2) | $C_{(11)}C_{(12)}C_{(7)}$ | 119,5(2) |
| $NC_{(3)}C_{(4)}$ | 103,6(2) | $C_{(6)}C_{(7)}C_{(8)}$ | 116,4(2) | | |

TABLE 4. Chemical Shifts and Coupling Constants in the PMR Spectra of Isomers (I) and (II)

| Iso-mer | δ, ppm | | | | | | $J$, Hz | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | 3-H | 5-H | 4-H | 4'-H | CH₃ | OCH₃ | 3,4 | 3,4' | 5,4 | 5,4' | 3,5 | 5, CH₃ | 4,4' |
| I | 5,89 | 3,91 | 2,69 | 1,92 | 1,32 | 3,50 | 7,17 | 3,74 | 6,61 | 9,64 | — | 6,00 | −13,03 |
| II | 5,87* | 4,60 | 2,40 | 2,06 | 1,06 | 3,49 | 2,08 | 6,25 | 6,55 | 6,23 | 0,62 † | 6,24 | −12,95 |

*Overlapped the 3-H signal for isomer (I).
†The sign of the constant was not found.

TABLE 5. Coordinates (×10⁴) and Equivalent Iso-tropic Temperature Factors $B_{eq}^{iso}$ (Å²) for Nonhydrogen Atoms

| Atom | $x$ | $y$ | $z$ | $B_{eq}^{iso}$ |
|---|---|---|---|---|
| O₍₁₎ | −32(1) | 7256(1) | 1228(2) | 3,96(5) |
| O₍₂₎ | −454(2) | 9220(1) | 1806(2) | 5,33(6) |
| O₍₃₎ | 3362(2) | 8461(1) | 1787(2) | 5,17(6) |
| N | 1011(2) | 7973(1) | 1664(2) | 3,70(5) |
| C₍₁₎ | −2439(3) | 6825(2) | −910(4) | 7,0(1) |
| C₍₂₎ | 762(3) | 9633(2) | 3115(3) | 6,5(1) |
| C₍₃₎ | 114(3) | 8741(1) | 828(3) | 4,36(7) |
| C₍₄₎ | −1306(3) | 8361(2) | −543(3) | 5,70(9) |
| C₍₅₎ | −1008(3) | 7398(1) | −452(3) | 4,67(7) |
| C₍₆₎ | 2537(2) | 7843(1) | 1767(2) | 3,57(6) |
| C₍₇₎ | 3159(2) | 6940(1) | 1949(2) | 3,33(6) |
| C₍₈₎ | 4184(2) | 6751(1) | 1200(3) | 4,11(7) |
| C₍₉₎ | 4858(3) | 5941(2) | 1363(3) | 5,31(9) |
| C₍₁₀₎ | 4555(3) | 5331(1) | 2291(3) | 5,78(9) |
| C₍₁₁₎ | 3556(3) | 5516(1) | 3042(3) | 5,56(9) |
| C₍₁₂₎ | 2845(2) | 6323(1) | 2871(3) | 4,34(7) |

TABLE 6. Coordinates (×10³) and Isotropic Temperature Factors $B^{iso}$ (Å²)

| Atom | $x$ | $y$ | $z$ | $B^{iso}$ | Atom | $x$ | $y$ | $z$ | $B^{iso}$ |
|---|---|---|---|---|---|---|---|---|---|
| H₍₁.₁₎ | −309(3) | 702(2) | −16(4) | 11,0(9) | H₍₄.₂₎ | −141(3) | 860(2) | −150(3) | 8,5(7) |
| H₍₁.₂₎ | −309(3) | 693(2) | −196(3) | 9,1(7) | H₍₅₎ | −32(2) | 722(1) | −103(2) | 5,6(5) |
| H₍₁.₃₎ | −215(3) | 624(2) | −73(3) | 7,7(6) | H₍₈₎ | 442(2) | 717(1) | 59(2) | 5,1(5) |
| H₍₂.₁₎ | 147(3) | 994(2) | 276(3) | 9,4(7) | H₍₉₎ | 554(2) | 584(1) | 81(2) | 6,0(5) |
| H₍₂.₂₎ | 24(3) | 1000(2) | 356(3) | 9,6(7) | H₍₁₀₎ | 504(3) | 479(1) | 245(3) | 6,5(5) |
| H₍₂.₃₎ | 143(3) | 923(2) | 397(3) | 9,0(7) | H₍₁₁₎ | 335(2) | 516(1) | 365(2) | 5,8(5) |
| H₍₃₎ | 91(2) | 910(1) | 58(2) | 4,1(4) | H₍₁₂₎ | 218(2) | 645(1) | 345(2) | 4,7(4) |
| H₍₄.₁₎ | −226(3) | 850(1) | −39(3) | 7,1(6) | | | | | |

($\lambda_{MoK_\alpha}$, θ/2θ scanning, graphite monochromator, θ ≤ 28°). The structure was calculated directly, and refined by the full-matrix least squares method in anisotropic approximation for all the nonhydrogen atoms. The Fourier difference synthesis gave all the hydrogen atoms, which were then refined in isotropic approximation. The final values of the divergence factors were R = 0.041 and $R_W$ = 0.040. All the calculations were carried out on an Eclipse S/200 computer using the INEXTL programs [12]. The coordinates of the nonhydrogen atoms are given in Table 5, and those of the hydrogen atoms in Table 6.

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# DEPENDENCE OF THE REACTIVITY OF FIVE-MEMBERED AROMATIC HETEROCYCLES ON THEIR STRUCTURE.

## 5.* PROTONATION OF FURAZANE, FUROXANE, AND THEIR AMINODERIVATIVES

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UDC 547.793.2.04:541.124.519.25

Proton affinity of furazane, furoxane, and their aminoderivatives for protonation at various centers was calculated by ab initio methods using the STO-3G basis set. Basicity was found to decrease in the following order: N-oxide oxygen atom, endocyclic nitrogen atom, amino group. The presence in the ring of aminogroups or N-oxide functions leads to elevated proton affinity of the basic centers which are located in the active positions of the ring.

Furazanes, furoxanes (furazane-N-oxide), and their aminoderivatives contain several potential protonation centers: the endocyclic nitrogen atoms, the amino group, and the N-oxide oxygen atom. Study of the acid-base properties of azoles, their N-oxides, and the aminoderivatives shows that, in principle, protonation can occur at any of these [2]. Besides this, experimental determination of the protonation site is encumbered with great difficulties since, for example, aminofurazanes and aminofuroxanes are weak bases and do not form stable salts with mineral acids. Therefore, we undertook a quantum mechanical study of the protonation of furazane, furoxane, and their aminoderivatives at various basic centers. The calculations were carried out nonempirically using the GAUSSIAN-76 program with the STO-3G minimal basis set according to the procedure described earlier [3]. The proton affinity (PA) was calculated as the difference of the total energies of the basic and protonated forms of the molecules (Table 1).

Optimization of the geometry, carried out by an MNDO method, showed that, in agreement with the x-ray structural analysis of 3-amino-4-methylfurazane [4], the amino group is pyramidal in aminofurazane itself and in aminofuroxanes. Protonation at the α- (relative to the amino group) nitrogen atom or at the α-N-oxide oxygen atom leads to complete flattening of the amino group and coplanarity of it with the ring. This same tendency is also observed upon protonation at the β-nitrogen atom or the β-N-oxide oxygen atom. However, in this case the amino group nevertheless retains some pyramidal character with an approximately coplanar disposition of the amino group and the ring.

Table 1 shows that the endocyclic nitrogen atom which is next to the amino group has the highest PA in aminofurazane. Its PA is much larger than for the ring nitrogen in unsubstituted furazane. An analogous increase of basicity of the endocyclic nitrogen atom upon intro-

*For Communication 4, see [1].