CHEMISTRY OF 1,1,2,2-TETRACYANOETHANE.

11.* SYNTHESIS AND STEREOCHEMICAL CHARACTERISTICS OF 3-METHYL-5-OXO-2'-AMINO-5'-PHENYL -3',4',4'-TRICYANOISOXAZOLINE-4-SPIRO-1'-CYCLOPENT-2'-ENE

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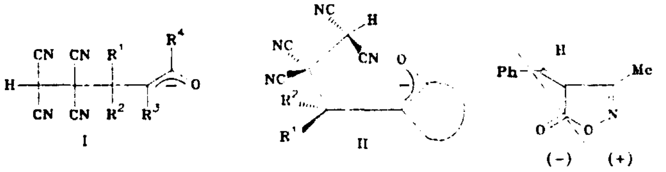
The Michael condensation of 1,1,2,2-tetracyanoethane with 3-methyl-4-benzylideneisoxazolin-5-one having the Z configuration leads to a heterocyclic spiran with retention of the cis orientation of the phenyl and keto groups. The deviations of the series of bond angles of the spiran from the standard values, the abnormal lengths of the C–C bonds adjacent to the gem-dicyano group, and the appearance of nonbonding $>C=O(\ldots)C\equiv N$ interactions and conjugation effects in the enaminonitrile fragment are discussed.

The Michael condensation of 1,1,2,2-tetracyanoethane (TCET) with α,β-unsaturated ketones and aldehyde [2-4] leads to various products: 3-amino-4,7,7-tricyano-2-oxabicyclo[2.2.1] heptanes; 2,6-diamino-1,5-dicyanobicyclo[3.3.0]oct-2,6-dienes; 1,8-dialkyl(aryl)-4,4,5,5-tetracyanooctane-1,8-diones; 2-amino-1,5,5-tricyano-1-cyclopentenes. The reactions are regioselective; each enone corresponds to one specific product. The direction of the reactions is controlled [5] either by the conformational stereoelectronic situation in the intermediate enolate anion (I) or by the thermostability of the intermediate (II), containing a cyclic π-conjugated system. In the present work we describe the synthesis and the stereochemical and structural characteristics of the spiran (III), produced in the reaction of TCET with 3-methyl-4-benzylideneisoxazolin-5-one.

Scheme



The configuration of the isoxazoline was established on the basis of the ASIS effect [6-9], according to which replacement of an aliphatic solvent by an aromatic solvent leads to an upfield shift of the proton signal.† Preferred solvation of the aromatic system takes place on the side of the lowest electron density in the molecule, and for a compound with a ketone group (isoxazoline) the location of the hydrogen in the (+)-region leads to its screening, while location in the (–)-region leads to descreening.‡ Since $\delta_{CDCl_3}(H) - \delta_{C_6H_6}(H) = 0.31$ ppm (see the experimental section), the isoxazoline has the Z configuration.

In the molecule of (III) (Fig. 1) the phenyl substituent is in the pseudoequatorial position and passes through the bisecting plane of the $C_{(2)}C_{(8)}C_{(7)}$ angle (torsion angle $\tau\ C_{(13)}C_{(12)}C_{(8)}H_{(3)} \approx 180°$). The ketone group occupies the pseudoaxial position, while the methyl group occupies the pseudoequatorial position in relation to the cyclopentene.

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*For Communication 10, see [1].

†An attempt to determine the configuration by x-ray crystallographic analysis was unsuccessful (see the experimental section).

‡In the scheme the boundary of the (+)- and (–)-regions is shown by the dotted line.

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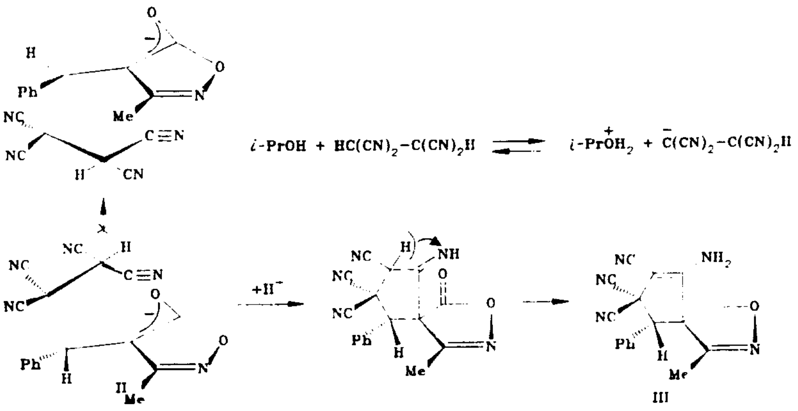
TABLE 1. Atomic Coordinates in the Molecule of (III) (× 10^4 for the nonhydrogen atoms, × 10^3 for the hydrogen atoms)

Atom	x	y	z	Atom	x	y	z
$O_{(1)}$	6200(1)	5337(2)	5106(2)	$C_{(12)}$	6789(1)	9161(2)	784(2)
$O_{(2)}$	6952(1)	6748(2)	5991(2)	$C_{(13)}$	6229(1)	10077(2)	2304(3)
$N_{(1)}$	6341(1)	4159(2)	3171(3)	$C_{(14)}$	5487(1)	11638(3)	1855(4)
$N_{(2)}$	8727(1)	2954(2)	4223(2)	$C_{(15)}$	5298(1)	12300(3)	−95(4)
$N_{(3)}$	10734(1)	4910(3)	2582(3)	$C_{(16)}$	5843(2)	11423(3)	−1601(4)
$N_{(4)}$	8111(1)	9919(2)	3997(3)	$C_{(17)}$	6587(1)	9849(2)	−1176(3)
$N_{(5)}$	9333(1)	9401(2)	−1977(3)	$H_{(1)}$	835(1)	229(3)	441(3)
$C_{(1)}$	7067(1)	4663(2)	2208(2)	$H_{(2)}$	932(1)	241(3)	445(3)
$C_{(2)}$	7525(1)	5724(2)	2792(2)	$H_{(3)}$	791(1)	707(2)	−17(2)
$C_{(3)}$	6892(1)	6038(2)	4796(3)	$H_{(4)}$	634(1)	962(3)	375(3)
$C_{(4)}$	7393(1)	3910(3)	366(3)	$H_{(5)}$	510(2)	1232(4)	296(4)
$C_{(5)}$	8500(1)	4708(2)	3156(2)	$H_{(6)}$	475(2)	1344(4)	−37(4)
$C_{(6)}$	9035(2)	5845(2)	2399(2)	$H_{(7)}$	573(2)	1188(3)	−308(4)
$C_{(7)}$	8479(1)	7805(2)	1495(2)	$H_{(8)}$	701(1)	922(3)	−224(3)
$C_{(8)}$	7626(1)	7498(2)	1112(2)	$H_{(9)}$	807(1)	310(3)	34(3)
$C_{(9)}$	9968(1)	5346(2)	2520(2)	$H_{(10)}$	697(1)	321(3)	40(3)
$C_{(10)}$	8248(1)	9004(2)	2924(3)	$H_{(11)}$	735(2)	495(3)	−86(4)
$C_{(11)}$	8968(1)	8699(2)	−467(3)				

Thus, the cis orientation of the phenyl and ketone groups is preserved in the molecule of (III), as also in the molecule of the initial isoxazoline, i.e., the cyclization (II → III) takes place without rotation of the 1,1,2,2-tetracyanopropyl fragment about the exo-C–C bond of the anion of compound (II).



The cyclopentene ring in the molecule of (III) is characterized by the envelop conformation with a folding angle of 150.2° along the $C_{(2)} \ldots C_{(7)}$ line. The dihedral angle between the planes of the isoxazoline ring and $C_{(2)}C_{(5)}C_{(6)}C_{(7)}$ amounts to 81.2°. The molecule of (III) is sterically overloaded, as shown by a series of intramolecular C...C and C...H contacts significantly less than the sums of the van der Waals radii of the atoms (3.4 and 2.9 Å respectively [10]): $C_{(13)} \ldots C_{(3)}$ 3.098(2), $C_{(13)} \ldots C_{(10)}$ 3.127(2), $H_{(4)} \ldots C_{(3)}$ 2.60(2), $C_{(17)} \ldots H_{(3)}$ 2.50(2) Å. In all probability the steric hindrances experienced by the C_{13} and $H_{(4)}$ atoms are more significant than the analogous hindrances for $C_{(17)}$, and this leads to substantial distortion of the bond angles (Table 1) at $C_{(12)}$ and $C_{(8)}$: $\angle C_{(8)}C_{(12)}C_{(13)} = 124.0(2)° > \angle C_{(8)}C_{(12)}C_{(17)} = 117.4(1)°$; $\angle C_{(12)}C_{(8)}C_{(2)} = 119.6(1)°$ and $\angle C_{(12)}C_{(8)}C_{(7)} = 117.3(2)° > \angle C_{(12)}C_{(8)}H_{(3)} = 109.6(8)°$. The stronger repulsions of the cis-orientated Ph and CN groups [$C_{(12)} \ldots C_{(10)}$ 3.049(2) Å] compared with the trans-orientated groups [$C_{(12)} \ldots C_{(11)}$ 3.242(2) Å] leads to inequality in the bond angles: $\angle C_{(8)}C_{(7)}C_{(10)} = 114.5(1)° > \angle C_{(8)}C_{(7)}C_{(11)} = 109.7(1)°$. The spiro link is characterized by a wide range of variation in the bond angles at the $C_{(2)}$ atom [99.8(1) ... 116.1(1)°] and by increase in the length of the $C_{(2)}$–$C_{(8)}$ [1.563(1) Å)] compared with the standard $C_{(sp^3)}$–$C_{(sp^3)}$ (1.534 Å) ([11], p. 66).

The increase in the length of the $C_{(7)}$–$C_{(8)}$ bond [1.574(2) Å] is typical of gem-dicyano-substituted $C_{(sp^3)}$–$C_{(sp^3)}$ bonds (see [12] and the references therein). It is curious that the gem-dicyano group has no effect at all on the length of the $C_{(sp^3)}$–$C_{(sp^2)}$ bond between the $C_{(6)}$–$C_{(7)}$ atoms [1.521 (2) Å], which corresponds to the standard value [13]. The enaminonitrile fragment is practically planar, and the maximum angle of twist in relation to the

TABLE 2. Bond Lengths l in the Molecule of (III)

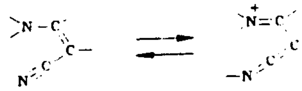
Bond	l, Å	Bond	l, Å	Bond	l, Å
$O_{(1)}$—$N_{(1)}$	1,454(2)	$C_{(2)}$—$C_{(5)}$	1,516(2)	$C_{(8)}$—$H_{(3)}$	0,99(2)
$O_{(1)}$—$C_{(3)}$	1,351(2)	$C_{(2)}$—$C_{(8)}$	1,563(1)	$C_{(12)}$—$C_{(13)}$	1,397(2)
$O_{(2)}$—$C_{(3)}$	1,194(2)	$C_{(4)}$—$H_{(9)}$	1,03(2)	$C_{(12)}$—$C_{(17)}$	1,392(2)
$N_{(1)}$—$C_{(1)}$	1,275(2)	$C_{(4)}$—$H_{(10)}$	1,02(3)	$C_{(13)}$—$C_{(14)}$	1,390(2)
$N_{(2)}$—$C_{(5)}$	1,335(1)	$C_{(4)}$—$H_{(11)}$	0,99(2)	$C_{(13)}$—$H_{(4)}$	1,00(2)
$N_{(2)}$—$H_{(1)}$	0,92(2)	$C_{(5)}$—$C_{(6)}$	1,362(2)	$C_{(14)}$—$C_{(15)}$	1,378(3)
$N_{(2)}$—$H_{(2)}$	0,90(2)	$C_{(6)}$—$C_{(7)}$	1,521(1)	$C_{(14)}$—$H_{(5)}$	1,01(2)
$N_{(3)}$—$C_{(9)}$	1,150(2)	$C_{(6)}$—$C_{(9)}$	1,410(2)	$C_{(15)}$—$C_{(16)}$	1,368(3)
$N_{(4)}$—$C_{(10)}$	1,138(2)	$C_{(7)}$—$C_{(8)}$	1,574(2)	$C_{(15)}$—$H_{(6)}$	1,01(2)
$N_{(5)}$—$C_{(11)}$	1,140(2)	$C_{(7)}$—$C_{(10)}$	1,486(2)	$C_{(16)}$—$C_{(17)}$	1,394(2)
$C_{(1)}$—$C_{(2)}$	1,507(2)	$C_{(7)}$—$C_{(11)}$	1,485(2)	$C_{(16)}$—$H_{(7)}$	1,03(3)
$C_{(1)}$—$C_{(4)}$	1,482(2)	$C_{(8)}$—$C_{(12)}$	1,508(2)	$C_{(17)}$—$H_{(8)}$	0,98(2)
$C_{(2)}$—$C_{(3)}$	1,517(2)				

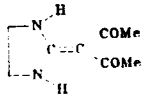
TABLE 3. Bond Angles in the Molecule of (III)

Angle	ω°	Angle	ω°	Angle	ω°
$O_{(1)}N_{(1)}C_{(1)}$	108,3(2)	$H_{(10)}C_{(4)}H_{(11)}$	109(2)	$N_{(5)}C_{(11)}C_{(7)}$	179,1(2)
$H_{(1)}N_{(2)}C_{(5)}$	1,19(1)	$N_{(2)}C_{(5)}C_{(2)}$	120.6(2)	$C_{(8)}C_{(12)}C_{(13)}$	124,0(2)
$H_{(1)}N_{(2)}H_{(2)}$	122(2)	$N_{(2)}C_{(5)}C_{(6)}$	127.9(2)	$C_{(8)}C_{(12)}C_{(17)}$	117,4(1)
$H_{(2)}N_{(2)}C_{(5)}$	117(1)	$C_{(2)}C_{(5)}C_{(6)}$	111.4(1)	$C_{(13)}C_{(12)}C_{(17)}$	118,6(1)
$C_{(2)}C_{(1)}N_{(1)}$	113,4(2)	$C_{(5)}C_{(6)}C_{(7)}$	111.1	$C_{(12)}C_{(13)}C_{(14)}$	120,3(2)
$C_{(2)}C_{(1)}C_{(4)}$	125,6(2)	$C_{(5)}C_{(6)}C_{(9)}$	125.8(1)	$C_{(12)}C_{(13)}H_{(4)}$	122(1)
$N_{(1)}C_{(1)}C_{(4)}$	121,0(2)	$C_{(7)}C_{(6)}C_{(9)}$	123.0(2)	$C_{(14)}C_{(13)}H_{(4)}$	118(1)
$C_{(1)}C_{(2)}C_{(3)}$	99,8(1)	$C_{(6)}C_{(7)}C_{(8)}$	102.1(1)	$C_{(13)}C_{(14)}C_{(15)}$	120,3(2)
$C_{(1)}C_{(2)}C_{(5)}$	116,1(1)	$C_{(6)}C_{(7)}C_{(10)}$	110.6(1)	$C_{(13)}C_{(14)}H_{(5)}$	120(1)
$C_{(1)}C_{(2)}C_{(8)}$	113,1(1)	$C_{(6)}C_{(7)}C_{(11)}$	113.6(1)	$C_{(15)}C_{(14)}H_{(5)}$	120(1)
$C_{(3)}C_{(2)}C_{(5)}$	109,5(1)	$C_{(8)}C_{(7)}C_{(10)}$	114.5(1)	$C_{(14)}C_{(15)}C_{(16)}$	120,1(2)
$C_{(3)}C_{(2)}C_{(8)}$	116,1(1)	$C_{(8)}C_{(7)}C_{(11)}$	109.7(1)	$C_{(14)}C_{(15)}H_{(6)}$	119(2)
$C_{(5)}C_{(2)}C_{(8)}$	102,8(1)	$C_{(10)}C_{(7)}C_{(11)}$	106.6(2)	$C_{(16)}C_{(15)}H_{(6)}$	122(2)
$O_{(1)}C_{(3)}C_{(2)}$	108,6(2)	$C_{(2)}C_{(8)}C_{(7)}$	103.5(1)	$C_{(15)}C_{(16)}C_{(17)}$	120,4(2)
$O_{(1)}C_{(3)}O_{(2)}$	122,2(2)	$C_{(2)}C_{(8)}C_{(12)}$	119.6(1)	$C_{(15)}C_{(16)}H_{(7)}$	123(1)
$O_{(2)}C_{(3)}C_{(2)}$	129,2(2)	$C_{(2)}C_{(8)}H_{(3)}$	104.8(9)	$C_{(17)}C_{(16)}H_{(7)}$	117(1)
$C_{(1)}C_{(4)}H_{(9)}$	109(2)	$C_{(7)}C_{(8)}C_{(12)}$	117.3(2)	$C_{(12)}C_{(17)}C_{(16)}$	120,3(2)
$C_{(1)}C_{(4)}H_{(10)}$	136(1)	$C_{(7)}C_{(8)}H_{(3)}$	100(1)	$C_{(12)}C_{(17)}H_{(8)}$	117(1)
$C_{(1)}C_{(4)}H_{(11)}$	96(2)	$C_{(12)}C_{(8)}H_{(3)}$	109.6(8)	$C_{(16)}C_{(17)}H_{(8)}$	122(1)
$H_{(9)}C_{(4)}H_{(10)}$	114(2)	$N_{(3)}C_{(9)}C_{(6)}$	178.1(2)	$C_{(3)}O_{(1)}N_{(1)}$	109,8(1)
$H_{(9)}C_{(4)}H_{(11)}$	109(2)	$N_{(4)}C_{(10)}C_{(7)}$	176.9(2)		

double bond amounts to 7° ($\tau C_{(7)}C_{(6)}C_{(5)}C_{(2)}$). The $N_{(2)}$—$C_{(5)}$ and $C_{(6)}$—$C_{(9)}$ bonds are shorter [1.335(1) and 1.410(2) Å)], while the $C_{(5)}{=}C_{(6)}$ bond is longer [(1.362(2) Å)] than the analogous bonds in enamines (N—C 1.38 ... 1.40 Å, C=C 1.33 ... 1.35 Å [14]) and acrylonitrile ($C_{(sp^2)}$—$C_{(sp)}$ 1.438 A [15]).

Thus, as in the previous investigations of enaminonitriles (see [16] and the references in the present work), a significant contribution from the bipolar form is observed in the NH_2—C=C—CN fragment. We note that the introduction of a second donor and an acceptor into the ethylene group, as occurs in compound (IV), will lead to a C=C bond length of 1.451(3) Å, i.e., to the appearance of the push-pull effect [17].





IV

According to the data from x-ray crystallographic investigations [18, 19], monocyclic isoxazolines are characterized by a conformation of the envelope type with projection of the carbon atom at position 5 from the plane of the remaining atoms of the ring. The acoplanar structure of isoxazolines is due to a number of factors, i.e., the ineffective $n_p(O)$—$\pi^*(N{=}C)$ interaction† and the tendency for the overlap and repulsion of n(N) and $n_\sigma(O)$ to decrease and also for the eclipsing of the endo and exo bonds in the Newman projections O → N and $C_{(3)}$ → $C_{(4)}$ to decrease. In bicyclic systems containing isoxazolines [20, 21] the confor-

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†In $\pi^*(N{=}C)$ the antibonding orbital is localized mainly at the carbon atom, and the overlap of the unshared electron pair of the oxygen with $\pi^*(C{=}N)$ is consequently insignificant.

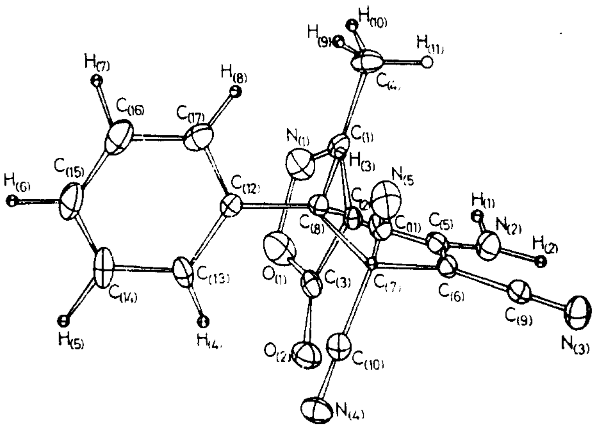
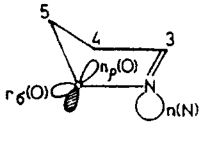
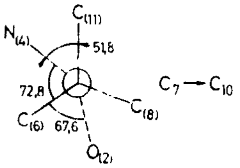


Fig. 1. The molecule of compound (III) with the 30% probability ellipsoids of the thermal vibrations for the nonhydrogen atoms.

mation of the latter is different and is, as a rule, due to the minimum steric strains in the molecule.

In (III) the introduction of the keto group at position 5 of the isoxazoline ring leads to its planarization. The length of the C=N bond 1.275(2) Å corresponds to the length of the analogous bond in isoxazolines [18-20] (1.27 ... 1.28 Å), whereas the O—N bond is approximately 0.02 ... 0.03 Å longer.





In all probability, the main reasons for the increase in the length of the bonds are the maximum overlap and repulsion of n(N) and n_σ(O) in (III), the eclipsing of the bonds in the planar ring, and the ineffective conjugation between n_p(O) and the amine group compared with the carbonyl.† It is curious that the O—$C_{(sp^3)}$ bond (O-alkyl) of 1.45 ... 1.46 Å [23] in the acyclic esters is also increased in length in comparison with the analogous bond in the ether in the absence of n_p(O)—π*(C=O) interaction.

In the molecule of (III) there is weak stabilizing nonbonding $O_{(2)}$ ... $C_{(10)}$ interaction [3.159(3) Å]. According to [24], experimental evidence for the coordination at the nitrile group is provided by the substantial distortion of the C—C≡N angle from 180°C [in compound (III) [$\angle C_{(7)}C_{(10)}N_{(4)}$ = 176.9(2)°], by the deflection of the atom from the nucleophile which coordinates it, by the coplanar arrangement of the nucleophile and the bent C—C≡N group (the sum of the angles $O_{(2)}C_{(10)}N_{(4)}$, $O_{(2)}C_{(10)}C_{(7)}$ and $N_{(4)}C_{(10)}C_{(7)}$ is 358.2°), and by the coordination of the donor at the triple bond at an angle somewhat larger than 90°[$\angle O_{(2)}C_{(10)}N_{(4)}$ = 92.7(1)°]. It should be noted that the interaction is promoted by the "rigid" geometry of (III). Thus, the dihedral angle between the isoxazoline plane, where the $n_pO_{(2)}$ orbital is located, and the $C_{(7)}C_{(10)}N_{(4)}$ plane is only 22.9°, which indicates interaction not only of electrostatic but also of orbital nature [25].

We note that the conformation of the cyclopentene in the crystal must also be preserved in the solution, since during the conversion the 1,3-diaxial interaction CH_3 ... CN ($C_{(4)}$ ... $C_{(11)}$) must, first, be stronger than the > C=O ... CN interaction (the CH_3 group is larger than the ketone group) and, second, the interactions are repulsive in nature and consequently destabilize the converted cyclopentene structure.

The crystal structure contains $N_{(4)}$ ... $H_{(1)}^{\dagger}$—$N_{(2)}^{\dagger}$ hydrogen bonds, which link the molecules into chains directed along the y axis. The structural parameters of the hydrogen

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†The decrease in the energy level of π*(C=O) compared with π*(C=N) [22] and the predominance of the contribution from the AO of the carbon to π*(C=X) leads to substantial predominance of the n_p(O)—π*(C=O) interaction compared with the n_p(O)—π*(N=C) interaction.

bonds are as follows: $N_{(2)}^{\dagger} \ldots N_{(4)}$ 3.003(3) Å, $H_{(1)}^{\dagger} \ldots N_{(4)}$ 2.19(2) Å, $\angle N_{(4)} \ldots H_{(1)}^{\dagger}N_{(2)}^{\dagger}$ = 150(2)°, $\angle H_{(1)}^{\dagger} \ldots N_{(2)}C_{(10)}$ = 149(2)°.

EXPERIMENTAL

The IR spectra were recorded in Vaseline oil on a UR-20 spectrometer. The PMR spectra were recorded on an RYa-2305 instrument at 60 MHz with HMDS as standard. The x-ray crystallographic investigation was conducted on an RÉD-4 automatic four-cicle diffractometer. The structure was interpreted by means of the Rentgen-75 program [26]. The TCET was obtained according to [27].

<u>3-Methyl-5-oxo-2'-amino-5'-phenyl-3'-4',4'-tricyano-oxazoline-4-spiro-1'-cyclopent-2'-ene (III).</u> A suspension containing 6.5 g (50 mmole) of TCET and 9.35 g (50 mmole) of 3-methyl-4-benzylideneisoxazolin-5-one in 150 ml of isopropyl alcohol was heated at 60°C. After 20 min both components had dissolved. After 2 h the precipitate was filtered off and washed with isopropyl alcohol. The product was recrystallized from a 1:1 mixture of acetonitrile and isopropyl alcohol; mp 230 ... 233°C (decomp.). The yield was 9 g (57%). IR spectrum ν_{NH} 3455, 3355, 3300, 3245, 3220; $\nu_{C\equiv N}$ 2265, 2220; $\nu_{C=C}$ 1650, $\nu_{C=N}$ 1615; $\nu_{C=O}$ 1785 cm^{-1}. Found %: C 64.2; H 3.6; N 21.9%. $C_{17}H_{11}N_5O_2$. Calculated: C 64.3; H 3.5; N 22.1%.

<u>X-Ray Crystallographic Investigation of Compound (III).</u> The colorless transparent crystals had the form of oblique-angled parallelepipeds and belonged to the triclinic system. The principal crystallographic data were as follows: $C_{17}H_{11}N_5O_2$, M = 317.31, a = 15.936(4), b = 8.027(2), c = 7.021(2) Å, α = 71.55(2), β = 73.71(2), γ = 68.30(2)°, V = 777.77 $Å^3$, d_{calc} = 1.36 g/cm^3, Z = 2, space group $P\bar{1}$.

The intensities of 1854 reflections with $I \geq 2\sigma(I)$ were measured in the range of $3.0° < \theta < 63.6°$ with CuK_α radiation by the $\theta/2\theta$ method. Absorption was not taken into account (μ_{CuK_α} = 8.1 cm^{-1}). The hydrogen atoms were localized from R syntheses. The structure was refined by least-squares treatment in full-matrix approximation with inclusion of the anisotropy for the O,N, and C atoms and the isotropy for the hydrogen atoms to R = 0.044. The atomic coordinates, bond lengths, and bond angles are given in Tables 1-3. The diagram of the molecules was obtained by means of the ELLIPS program [28]. 3-Methyl-4-benzylideneisoxazolin-5-one was obtained according to the method in [29]. The configuration of the isoxazoline was initially determined from the data from x-ray crystallographic analysis of crystals grown in chloroform. The crystals were of poor quality, rhombic, with unit cell parameters: $a \approx 7.3$, b = 22.9, $c \approx 14.1$ Å. Our results did not agree with data from x-ray crystallographic investigation of the Z isomer of isoxazoline [30], in which the monoclinic form was established. Two variations are therefore possible: 1) The investigated isoxazoline has the E configuration; 2) the investigated isoxazoline has the Z configuration but, in contrast [29], exists in a different polymorphous modification. On account of the uncertainty the configuration of the isoxazoline was determined by means of the PMR spectra. PMR spectrum, δ (in benzene): 1.50 (CH_3), 6.71 (1H, s), 7.40 (5H, m, C_6H_5); (in deuterochloroform): 2 (CH_3), 7.02 (1H, s), 7.75 ppm (5H, m, C_6H_5).

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