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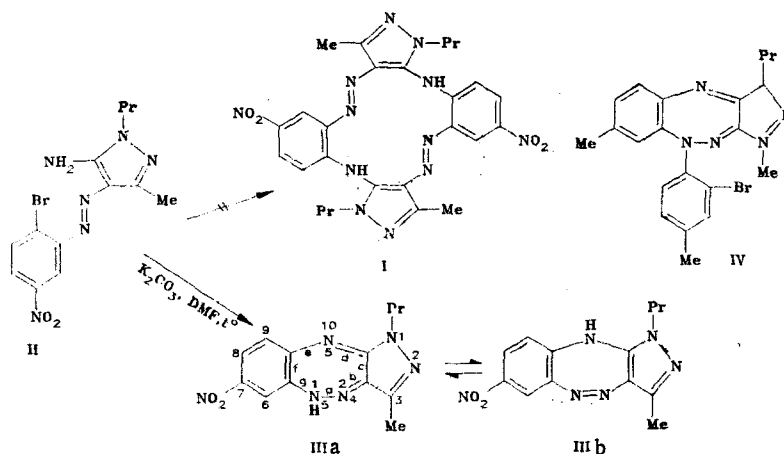
A NEW DERIVATIVE OF 1,5-DIHYDROPYRAZOLO[4,3-c][1,2,5]BENZOTRIAZEPINE

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A new compound, 1,5-dihydro-3-methyl-7-nitro-propylpyrazolo[4,3-c][1,2,5]benzotriazepine, was synthesized by intramolecular cyclization of 5-amino-4-[(2-bromo-5-nitrophenyl)azo]-3-methyl-1-isopropylpyrazole, and it was established on the basis of the spectral data that the triazepine ring in the synthesized compound exists in two tautomeric forms — amino-azo- and hydrazone. The structure of the compound synthesized was confirmed by the data of the PMR, IR, electronic, and mass spectra.

In an attempt to produce the macrocyclic ligand I by nontemplate bimolecular autocyclization of compound II, 1,5-dihydro-3-methyl-7-nitro-1-propylpyrazolo[4,3-c][1,2,5]benzotriazepine (III), a product of intramolecular cyclization, was isolated.

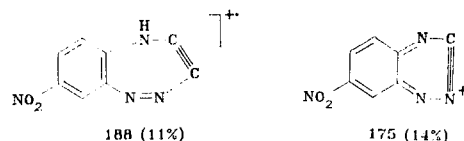


The formation of the derivative 1,5-dihydropyrazolo[4,3-c][1,2,5]-benzotriazepine IV as a side product was previously observed in the intermolecular autocyclization of 5-amino-4-[(2-bromo-4-methylphenyl)-azo]-3-methyl-1-propylpyrazole [1, 2]. The new triazepine derivative III does not contain substituents at the nitrogen atom in the hydrazone group.

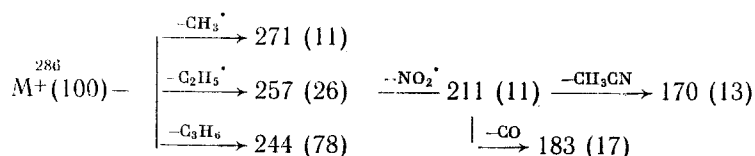
The pathways of decomposition of the molecular ions of triazepines III and IV are analogous. In the mass spectrum of compound III a peak of the molecular ion with m/z 286* is observed (100%). The seven-membered triazepine ring is stable; therefore at the first stage of the decomposition the pyrazole ring begins to break down, forming fragments characteristic of triazepine systems:

*Here and henceforth, the numbers characterizing an ion define the value of m/z .

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The decomposition of the pyrazole ring is paralleled by the usual fragmentation, associated with the splitting out of fragments of the propyl substituent in various sequences:



The presence of isobestic points (Fig. 1) in the electronic absorption spectra of solutions of the tautomers IIIa and IIIb in benzene, chloroform, and dimethyl sulfoxide (Table 1) indicates the existence of a tautomeric equilibrium in solution. As we go from weakly polar benzene to more polar solvents, disappearance of the weak absorption band at 693 nm is observed, with the appearance of a band at 540 nm. Instead of the band at 378 nm and its point of inflection at 450 nm, a band appears at 400 nm, and instead of a shoulder at 309 nm and a point of inflection at 345 nm, an intensive transition at 333-341 nm is sufficient.

The PMR spectra of solutions of the tautomers IIIa and IIIb in C_6D_6 , CDCl_3 and DMSO-D_6 (Table 2) at room temperature (or elevated temperature) as a result of rapid proton exchange between tautomeric forms exhibit an averaged picture. But even the averaged picture permits a characterization of the relative shift of the tautomeric equilibrium in the series of the indicated solvents. Thus, the chemical shift (CS) of the proton 9-H is shifted by 1.1 ppm from 5.48 in C_6D_6 to 6.59 ppm in DMSO-D_6 . This is evidently associated with the response of a shift of the tautomeric equilibrium from the aminoazo- to the hydrazone form, accompanied by replacement of the electron donor ortho-NH substituent by an electron acceptor sp^2 -hybridized nitrogen atom. Small shifts of the CS in the PMR spectra when C_6D_6 is replaced by a more polar solvent already occur as we go to CDCl_3 . This pertains not only to the proton 9-H (5.48 \rightarrow 6.11 ppm), but also the protons 3- CH_3 (1.51 \rightarrow 2.01 ppm) and N- CH_2 (2.93 \rightarrow 3.40 ppm). The predominance of the hydrazone tautomeric form IIIa in polar solvents is also evidence of closeness of the CS of the aromatic protons and the methyl group of the tautomer IIIa in solution in DMSO-D_6 to the CS of the corresponding protons in compound IV [1], considering the replacement of the nitro group by a methyl group and the shielding effect (+1.1 ppm) of the magnetic anisotropy of the N-phenyl ring in the triazepine IV on the 6-H proton.

The IR spectra of crystalline samples of the tautomers IIIa and IIIb (in KBr tablets), recrystallized from benzene (IIIb) and acetone (IIIa), differ appreciably from one another. In particular, the bands of the asymmetric and symmetrical stretching vibrations of the nitro group in the spectrum of the tautomer IIIb lies at 1519 (int.) and 1317 (very int.), while that of the tautomer IIIa lies at 1541 (med.) and 1307 cm^{-1} (very int.). The amino azo-form IIIb is also confirmed by the known dependence of the diameters of the band $\nu_{\text{asym}} \text{NO}_2$ on the polarity of the substituent in substituted nitrobenzenes 3, 4 (an increase in the intensity and decrease in the frequency of ν_{asym} of NO_2 under the influence of a para-electron donor substituent). Thus, the benzotriazepine III crystallizes from benzene and acetone chiefly in the form that predominates in solution with a large solvent; aminoazo- and hydrazone, respectively. The IR spectra indicated a transition to a more stable hydrazone form IIIa when the metastable crystalline form IIIb is subjected to prolonged storage.

The splitting of the band of the stretching vibration ν_{NH} (3424 (ϵ 41) and 3404 cm^{-1} (ϵ 38), as well as the bands of $\nu_{\text{asym}} \text{NO}_2$ 1533 and 1522 cm^{-1} (p) in the IR spectrum of the mixture of tautomers IIIa and IIIb in solution in CDCl_3 is evidently a consequence of tautomeric equilibrium. In benzene solution the mixture of tautomers IIIa and IIIb in which, according to the data of the PMR spectrum, the aminoazo form predominates, only the band ν_{NH} is observed at 3365 cm^{-1} .

In aqueous solutions the absorption spectra of compound III (Fig. 2) were recorded at various pH values of the medium. In the region of pH 9.0-11.0 there is a deprotonation,

TABLE 1. Electronic Absorption Spectra of Compounds III and IV

Compound	Solvent (temperature, °C)	$\lambda_{\max}(\lg \epsilon)$							
III	C ₆ D ₆ (60)	693 (2,544)				447P* (3,316)	378 (4,075)	345 P (3,933)	309 sh (3,842)
III	CDCl ₃ (30)	696 sh (2,000)				461 sh (2,161)	377 (3,924)	333 (4,208)	
III	DMSO-D ₆ (30)		572 P (3,230)	542 (3,342)	522 P (3,320)		401 (3,876)	341 (4,278)	
IV	CDCl ₃ [1]		585 (2,810)				405 (3,660)		

*p is a point of inflection; sh is a shoulder.

TABLE 2. PMR Spectra of Compounds III and IV

Compound	Solvent (temperature, °C)	Chemical shifts, ppm							
		CH ₂	CH ₂	NCH ₂	3-CH ₃	NH	6-H	8-H	9-H
III	C ₆ D ₆ (60)	0,70 t	1,32 m	2,93 t	1,51 s	*	†	†	5,48 d
III	CDCl ₃ (30)	0,92 t	1,70 m	3,40 t	2,01 s	*	7,44 d	7,59 dd	6,11 d
III	DMSO-D ₆ (30)	0,89 t	1,65 m	3,63 t	2,07 s	8,25 s	7,79 s	7,85 dd	6,59 d
IV	CDCl ₃ [1]	0,90 t	1,72 m	3,43 t	1,86 s	—	5,51 d	6,64 dd	6,50 d

*Not observed on account of proton exchange.

†The positions of the signals were not established on account of the low solubility and overlapping with the signal of the solvent.

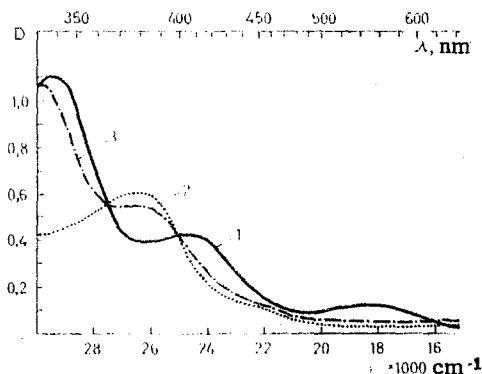


Fig. 1

Fig. 1. Electronic spectra of compound III: 1) in DMSO; 2) in benzene; 3) in CHCl₃; $\sim 10^{-4}$ M; $l = 0.5$ cm.

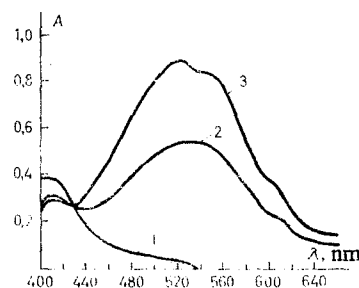


Fig. 2

Fig. 2. Absorption spectra of aqueous solutions of compound III: 1) pH 6.35; 2) pH 10.25; 3) pH 12.70; $8 \cdot 10^{-3}$ M; $l = 1.0$ cm.

which is accompanied by a distinct color change from yellow ($\lambda_{\max} = 405$ nm) to red ($\lambda_{\max} = 520$ nm).

EXPERIMENTAL

The mass spectra were obtained on a Varian MAT-311A mass spectrometer; a source of electron impact with direct introduction of the sample into the region of ionization, ionization energy 80 eV, was used. The PMR spectra of saturated (<0.05 M) solutions of compound III in C₆D₆ and CDCl₃ and an ~ 0.1 M solution in DMSO-D₆ were measured at 30°C on a Varian XL-100-12 spectrometer. The IR spectra (in KBr tablets or ~ 0.5 M solution in CDCl₃ in a 1-mm cuvette) were measured on a UR-20 spectrometer. The electronic absorption spectra ($\sim 10^{-4}$ M) of solutions of the tautomers IIIa and IIIb were measured on Specord UV-vis spectrophotometers (in benzene, chloroform, and DMSO) and on an SF-26 spectrophotometer (in water).

5-Amino-4-[(2-bromo-5-nitrophenyl)azo]-3-methyl-1-propylpyrazole (II) was produced according to [5], mp 291.0-202.0°C.

1,5-Dihydro-3-methyl-7-nitro-1-propylpyrazolo[4,3-c][1,2,5]benzotriazepine (IIIa, b). A mixture of 0.37 g (0.01 mole) compound II, 0.55 g (0.04 mole) potassium carbonate, and 100 ml DMFA was boiled for 3 h. The solvent was distilled off to dryness, the residue washed successively with CCl₄, benzene, and chloroform, dissolved in acetone, the solution applied on a glass filter (diameter 6.0 cm, height 6.0 cm, No. 3), filled to two thirds of the volume with aluminum oxide (alkaline, L 50/40), and eluted with a 1:2 mixture of benzene and acetone, under vacuum. The eluate of the corresponding brown zone was collected, evaporated to a volume of 50 ml, and left for crystallization. Yield 0.08 g (28.0%) of a crystalline substance, Mp 143.0-144.5°C; soluble in alcohol, acetone, DMFA, aqueous alkalies, acids, 25% aqueous ammonia; sparingly soluble in benzene chloroform, hexane, CCl₄; almost insoluble in water. Found: C 54.3; H 5.0; N 29.2%. C₁₃H₁₄N₆O₂. Calculated: C 54.5; H 4.9; N 29.4%; M 286.

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