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SYNTHESIS AND SOME CHEMICAL CONVERSIONS OF 2-([2,2]-5-PARA-CYCLOPHANYL)PYRROLE

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2-([2,2]-5-Paracyclophanyl)pyrrole has been synthesized and nitration and formylation of it have been effected. The 1-β-cyanoethyl derivative and 2-formyl-5-paracyclophanyl-3H-pyrrolizine have been obtained from 5-formyl-2-([2,2]-5-paracyclophanyl)pyrrole by the action of acrylonitrile and acrolein respectively under Michael reaction conditions.

Keywords: paracyclophane, pyrrole, heterocyclization, addition, Trofimov reaction.

The heterocyclization of ketoximes with acetylene in a superbasic medium (Trofimov reaction) is a simple and convenient method of obtaining substituted NH- and N-vinylpyrroles [1-3], tetrahydropyrrolo[3,2-*c*]-pyridines [4], and tetrahydropyrrolo[1,2-*c*]pyrimidines [5]. The heterocyclization of oximes of acetophenones substituted in the aromatic ring has been described, however oximes of acetyl substituted [2,2]paracyclophanes have not been studied in this reaction. It might have been expected that the paracyclophane fragment, due to its structure and large steric bulk, will prove to have a different influence than substituted phenyl on the course of the Trofimov reaction.

In the present work the heterocyclization of the oxime of 5-acetyl[2,2]paracyclophane (**1**) with acetylene in superbasic medium and some conversions of 2-([2,2]-5-paracyclophanyl)pyrrole (**2**) have been studied. The heterocyclization reaction was carried out in the systems KOH–DMSO and RbOH–DMSO at 85-110°C and atmospheric pressure. The reaction was accompanied by resinification. In KOH–DMSO the yield of substituted paracyclophane **2** was 16-22%, but its N-vinyl-substituted derivative **3** was not present in the reaction mixture. In addition to compound **2** the O-vinyl ether of oxime **1** (compound **4**) and 5-acetyl[2,2]paracyclophane were isolated (6-8% yield) from the reaction mixture. The latter is formed by retro-oxime fission of the initial oxime. Thus oxime **1** behaves analogously to acetophenone oxime and its *p*-chloro and *p*-amino-substituted derivatives on heterocyclization in the presence of KOH, where the corresponding O-vinyl ethers were isolated but N-vinylpyrroles were not present in the reaction mixtures [10].

In RbOH–DMSO the yield of pyrrole **2** was somewhat lower (9-14%), however in this case the N-vinylpyrrole **3** was obtained (6-8%), but the vinylic ether **4** was not present in the reaction mixture, since rubidium hydroxide is more reactive in the pyrrolization reaction and in the N-vinylation of pyrroles [11].

Certain chemical conversions of the newly synthesized pyrrole **2** have been studied, formylation according to Wilsmeier–Haack and nitration with copper nitrate in acetic anhydride according to Menke.

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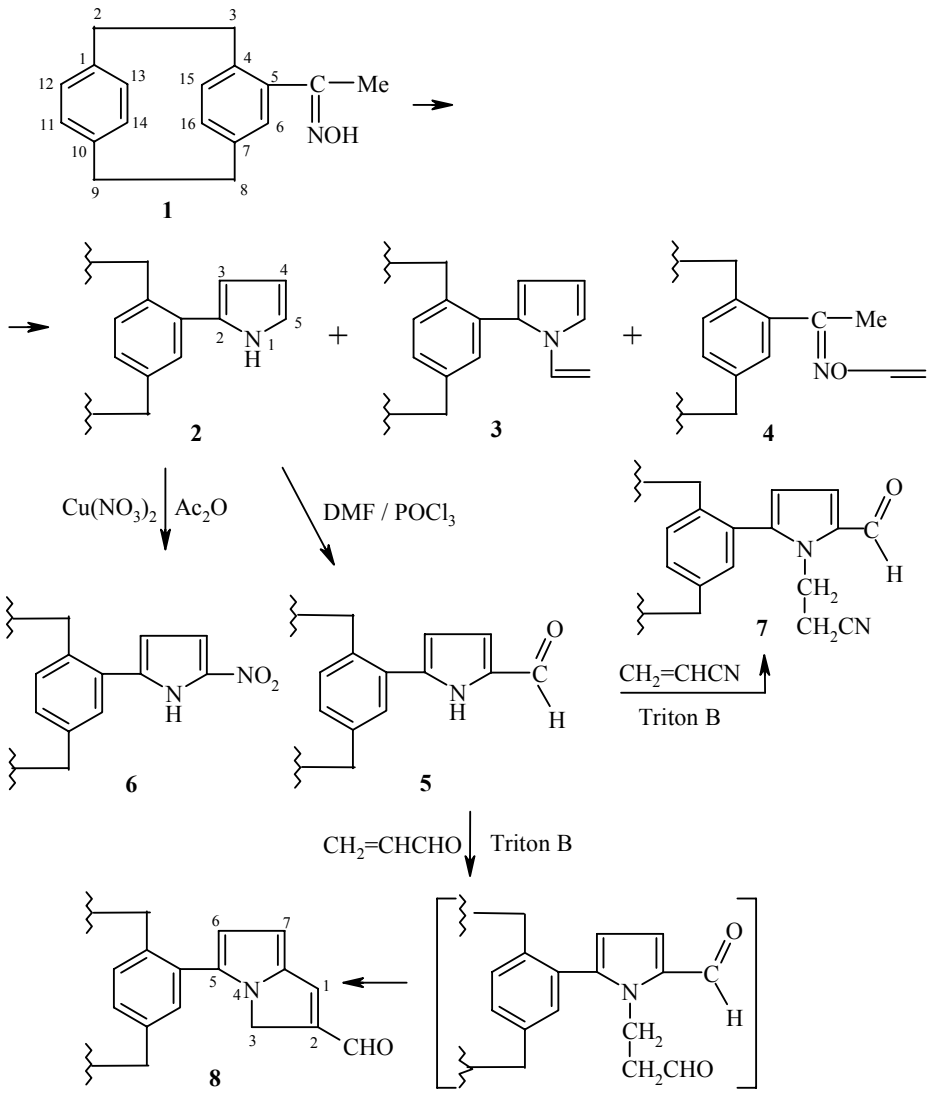


Both electrophilic substitution reactions proceeded at the α-position of the pyrrole ring. The 2-formyl substituted pyrrole **5** was obtained in 69% yield for which a 4 to 5-fold excess of phosphorus oxychloride was required. The nitro derivative **6** was obtained in significantly lower yield (13%) due to marked resinification of the reaction mixture.

On alkylation of pyrrole **2** with acrylonitrile under Michael reaction conditions in the presence of Triton B, 1-(β-cyanoethyl)-5-formyl-2-(2,2]-5-paracyclophanyl)-pyrrole **7** was obtained. In the case of acrolein the Michael addition adduct underwent further intramolecular cyclization into 2-formyl-5-([2,2]-5-paracyclophanyl)-3H-pyrrolizine (**8**). The possibility of intramolecular cyclization in the latter case is caused by the strong electron-withdrawing effect of the carbonyl group of the β-formylethyl fragment.

In the IR spectra of compounds **2**, **5**, and **6** there were bands for NH stretching vibrations at 3284-3434 cm^{-1}. The intense band for the CO stretching vibrations in compounds **5**, **7**, and **8** was displayed at 1660, 1646, and 1727 cm^{-1} respectively. The stretching vibrations of the NO_2 group in compound **6** and the CN group in compound **7** were observed at 1500, 1373, and 2260 cm^{-1} respectively.

Signals were present for all the required protons in the ^1H NMR spectra of compounds **1**-**8** (Table 1). A broadened signal was observed for the oxime group proton (8.9 ppm), a singlet for the methyl group protons (2.26 ppm), and complex multiplets for the aromatic and methylenic protons. The pyrrole ring in compound **2**

TABLE 1. ^{1}H NMR Spectra of [2,2]Paracyclophanyl-substituted Oximes **1**, **4**, Pyrroles **2**, **3**, **5-7**, and Pyrrolizine **8**

Com-pound	Chemical shifts, δ, ppm (coupling constants, *J*, Hz)					
	N–R	H–3	H–4	5–R[1]	paracyclophanyl	
					CH_2	Ar
1	8.9, br. s (OH)*	—	—	—	2.9-3.5, m	6.4-6.75, m
2	8.16, br. s (NH)	6.43, m, $J_{NH,3}$ = 2.5, $J_{3,4}$ = 3.4, $J_{3,5}$ = 1.5	6.37, m, $J_{NH,4}$ = 2.8, $J_{3,4}$ = 3.4, $J_{4,5}$ = 2.8	5-H, 6.91, m, $J_{NH,5}$ = 2.8, $J_{3,5}$ = 1.5, $J_{4,5}$ = 2.8	2.7-3.6, m	6.45-6.75, m
3	6.68, dd, 4.52, dd, 5.07, dd, *J* = 8.9; 15.9; 1.2 (N–CH=CH_2)	*[2]	*[2]	7.17, m	2.75-3.2, m	6.35-6.85, m
4	7.14, dd, 4.22, dd, 4.75 dd, *J* = 6.7; 14.3; 1.5 (O–CH=CH_2)*[3]	—	—	—	2.8-3.6, m	6.3-6.85, m
5	9.15, br. s (NH)	6.54, dd, $J_{NH,3}$ = 2.8, $J_{3,4}$ = 4.0	7.08, dd, $J_{NH,4}$ = 2.8, $J_{3,4}$ = 4.0	9.55, s (CHO)	2.6-3.25, m 3.45-3.7, m	6.4-6.65, m
6	9.27, br. s (NH)	6.51, dd, $J_{NH,3}$ = 2.8, $J_{3,4}$ = 4.3	7.27, dd, $J_{NH,4}$ = 2.8, $J_{3,4}$ = 4.3*[4]	—	2.65-3.25, m 3.4-3.6, m	6.4-6.7
7	2.39, m (CH_2); 4.27, td (H_B); 4.77, td (H_A), J_{AB} = 13.1, J_{ACH_2} = 6.9, J_{BCH_2} = 7.3 (N$CH_AH_BCH_2$CN)	6.61, d, $J_{3,4}$ = 3.4*[4]	7.18, d, $J_{3,4}$ = 4.3	9.85, s (CHO)	2.65-3.25, m	6.4-6.75, m
8	1-H 7.45, br. s*[5]	3-CH_AH_B 4.75, d, 4.40, d, $J_{A,B}$ = 20.5	6-H *[2]	7-H *[2]	2.85-3.20, m	6.4-6.8, m

* 2.26, s, Me.

*[2] Overlapped by signals of aromatic protons.

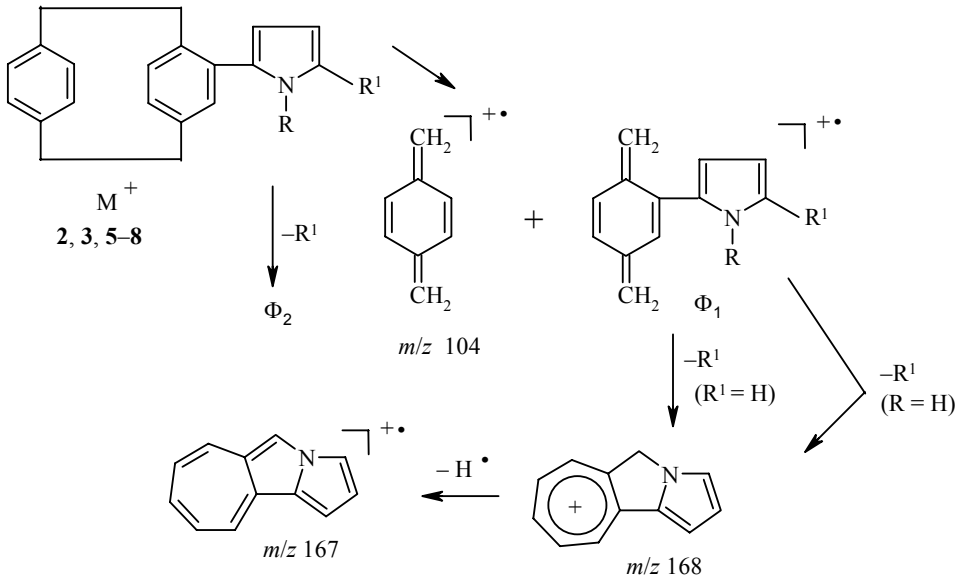
*[3] 2.25, s, Me.

*[4] Measured by the double resonance difference spectrum {4-H} or {NH}.

causes the appearance in its spectrum of a broadened signal for the NH proton (8.16 ppm), and three multiplets for the 3-H, 4-H, and 5-H protons with coupling constants characteristic of a pyrrole ring $J_{1,5}$ = 2.8, $J_{1,4}$ = 2.8, $J_{1,3}$ = 2.5, $J_{3,4}$ = 3.4, $J_{3,5}$ = 1.5, and $J_{4,5}$ = 2.8 Hz. Signals were recorded in the spectrum of the N-vinyl substituted derivative **3** for a three-spin system for the protons of the vinyl fragment with vicinal coupling constants J_{cis} = 8.9, J_{trans} = 15.9, and geminal $J_{cis,trans}$ = 1.2 Hz.

In the spectrum of O-vinyl ether **4** a singlet was present for the methyl group (2.25 ppm) and three double doublets for the O-vinyl fragment. The spectra of the 5-formyl and 5-nitro substituted compounds **5** and **6** were characterized by the absence of the H-5 signal, but the vicinal coupling constant between H-3 and H-4 was 4.0 (**5**) and 4.3 Hz (**6**). In the low field portion of the spectrum of these compounds broadened signals were observed for the NH protons at 9.15 (**5**) and 9.27 (**6**) and for the formyl group of compound **5** at 9.55 ppm. In difference to compound **5**, the broadened signal for the NH proton was absent from the spectrum of its N-β cyanoethyl derivative **7**, but three multiplets for the methylene protons were recorded at 4.77, 4.27, and 2.39 ppm with integrated intensities of 1H, 1H, and 2H respectively. The protons belonging to the first two multiplets have geminal coupling constant J = 13.1 Hz. In the spectrum of pyrrolizine **8** a singlet signal was observed at 9.70 ppm for the formyl proton, broadened due to long range coupling with the singlet for the H-1 proton at 7.45 ppm, and also two double doublet signals for the nonequivalent H-3 protons (δ_A 4.75, δ_B 4.40 ppm) with geminal coupling constant 20.5 Hz.

In the mass spectra of compounds **2**, **3**, **5-8** (Table 2) there were peaks of various intensities for the molecular ions.The main decomposition path of the M^+ ions of all the compounds is linked with the breakdown of the [2,2]paracyclophene fragment into two, as a result of which fragment ions are formed with *m/z* 104 and Φ_1. In the case of pyrroles **6-8,** having a functional group at $C_{(2)}$ of the pyrrole or pyrrolizine fragment, a second breakdown pathway for M^+ is linked with elimination of the functional group and the formation of fragment Φ_2.



On dissociation of the M^+ ion of compound **7** fission of CH_2CN was observed, characteristic of N-ethyl substituted pyrroles [12]. In the second stage of decomposition the Φ_1 ion eliminates either R or R^1 with the formation of a fragment ion with *m/z* 168, probably having the structure of a tropiliumpyrrolizine cation. This ion then eliminates H. In the case of the formyl and nitro-substituted pyrroles **5-7** the Φ_1 ion ejects CO and OH respectively.

TABLE 2. Fragment Ions in the Mass Spectra of Compounds **2**, **3**, **5-8**

Compound	*m/z* (I_{rel}, %)						
	M^+	104	Φ_1	Φ_2	168	167	Other ions
2	273 (30)	(100)	169 (38)		(100)	(25)	
3	299 (100)	(8)	195 (40)		(6)	(10)	$[\Phi_1–H]^+$ 194 (90)
5	301 (10)	(100)	197 (3)		(10)	(10)	$[\Phi_1–CO]^+$ 169 (10)
6	318 (8)	(100)	214 (4)	272 (46)	(31)	(23)	$[\Phi_1–OH]^+$ 197 (15)
7	354 (31)	(100)	250 (13)	326 (5)	(18.7)	(25)	$[\Phi_1–CO]^+$ 222 (35) $[\Phi_1–H]^+$ 249 (17) $[M–CH_2CN]^+$ 314 (5)
8	339 (3)	(31)	235 (4)	310 (5)	(15)	(13)	$[\Phi_2–HCO]^+$ 206 (7)

The molecular and crystal structures of 2-paracyclophanyl-1-vinylpyrrole **3** were established by X-ray structural analysis. The crystal structure of compound **3** contains two crystallographically independent molecules **A** and **B** packed together (see Fig. 1). The numbering of the atoms in the **A** and **B** molecules is the same. In Tables 3, 4 and 5 are given the coordinates of atoms, bond lengths, and valence angles existing in the **A** and **B** molecules. The paracyclophane fragment has the common geometric parameters for this system [13,14]. The deviation of the tertiary atoms $C_{(1)}$, $C_{(4)}$, $C_{(9)}$, and $C_{(12)}$ from the plane of the benzene rings was 0.16 Å, as for other [2,2]paracyclophanes.

As a result of this the benzene rings take on a boat configuration. The pyrrole ring is turned from the paracyclophane plane by 44.8° in molecule **A** and by 42.5° in molecule **B**. Molecules **A** and **B** differ in the angle of turn of the vinyl group relative to the pyrrole ring. The appropriate dihedral angle is 5.81° in molecule **A** and 22.83° in molecule **B**. The $C_{(21)}$=$C_{(22)}$ bond lengths in the vinyl group are 1.263(9) and 1.308(7) Å respectively, i.e. shorter than the length of this bond in alkenes. The $N_{(1)}$–$C_{(21)}$ bond lengths in both molecules were close to one another and were 1.414(5) and 1.410(5) Å, shorter than in amines (1.470 Å). This indicates the displacement of electron density from the pyrrole ring to the vinyl group. The X-ray structural analysis data correlate well with the data obtained from other physicochemical methods [1]. The pyrrole ring is flat, the α-β ($C_{(17)}$–$C_{(20)}$), α'-β' ($C_{(18)}$–$C_{(19)}$), and β-β' ($C_{(19)}$–$C_{(20)}$) bonds in the pyrrole rings of both molecules are shorter

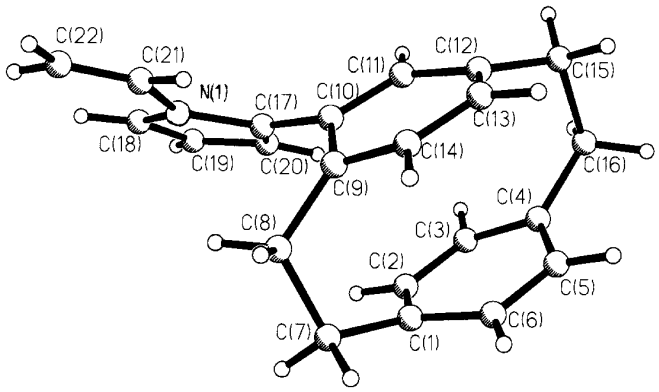


Fig. 1. General form of molecule **A** and numbering of atoms.

than in pyrrole (1.382 and 1.417 Å respectively). The lengths of the $N_{(1)}$-α and N_1-α' bonds were different in both molecules. The $N_{(1)}$–$C_{(17)}$ bond has the same length (1.370 Å), but the $N_{(1)}$–$C_{(18)}$ bond at 1.387(4)-1.384(4) Å, is longer than in pyrrole.

TABLE 3. Coordinates of Atoms in Fractions of the Unit Cell Axes and Thermal Corrections U_{iso} and U_{eq} for Compound **3**

Atom	*x*	*y*	*z*	U_{iso}/U_{eq}
1	2	3	4	5
		Molecule **A**		
N(1)	0.1533(2)	0.9276(1)	0.3113(2)	0.0617(7)
C(1)	0.2170(4)	0.8737(2)	-0.0114(2)	0.075(1)
C(2)	0.3130(4)	0.8658(3)	0.0425(3)	0.084(1)
C(3)	0.3622(4)	0.8028(4)	0.0547(3)	0.086(1)
C(4)	0.3185(3)	0.7431(3)	0.0126(3)	0.079(1)
C(5)	0.2395(3)	0.7544(3)	-0.0563 (3)	0.077(1)
C(6)	0.1905(4)	0.8182(3)	-0.0681(3)	0.076(1)
C(7)	0.1348(5)	0.9311(2)	0.0055(3)	0.094(1)
C(8)	0.0663(4)	0.9183(2)	0.0917(3)	0.071(1)
C(9)	0.0781(2)	0.8458(2)	0.1295(2)	0.0492(8)
C(10)	0.1580(2)	0.8288(2)	0.1991(2)	0.0447(7)
C(11)	0.1995(3)	0.7616(2)	0.2018(2)	0.0504(8)
C(12)	0.1654(3)	0.7107(2)	0.1413(2)	0.0606(9)
C(13)	0.0689(3)	0.7247(2)	0.0887(2)	0.0624(9)
C(14)	0.0273(3)	0.7906(2)	0.0830(2)	0.0567(9)
C(15)	0.2406(4)	0.6511(2)	0.1187(4)	0.092(1)
C(16)	0.3356(5)	0.6729(3)	0.0529(4)	0.105(2)
C(17)	0.2108(2)	0.8806(2)	0.2593(2)	0.0480(7)
C(18)	0.2288(3)	0.9662(2)	0.3629(3)	0.070(1)
C(19)	0.3321(3)	0.9449(2)	0.3434(3)	0.069(1)
C(20)	0.3221(3)	0.8915(2)	0.2797(2)	0.0564(8)
C(21)	0.0361(3)	0.9297(2)	0.3186(3)	0.086(1)
C(22)	-0.0171(5)	0.9710(4)	0.3678(5)	0.174(3)
H(2)	0.335(3)	0.904(2)	0.077(2)	0.07(1)
H(3)	0.415(3)	0.791(2)	0.101(3)	0.10(1)
H(5)	0.211(3)	0.715(2)	-0.091(2)	0.09(1)
H(6)	0.134(3)	0.823(2)	-0.110(2)	0.08(1)
H(71)	0.076(4)	0.930(2)	-0.056(4)	0.15(2)
H(72)	0.174(3)	0.978(2)	0.019(3)	0.12(1)
H(81)	-0.009(4)	0.926(2)	0.075(3)	0.12(2)
H(82)	0.084(3)	0.957(2)	0.144(2)	0.09(1)
H(11)	0.262(2)	0.750(1)	0.242(2)	0.057(8)
H(13)	0.045(3)	0.689(2)	0.048(2)	0.07(1)
H(14)	-0.032(3)	0.803(2)	0.037(2)	0.08(1)
H(151)	0.197(4)	0.617(2)	0.085(3)	0.13(2)
H(152)	0.281(4)	0.632 (2)	0.179(3)	0.13(2)
H(161)	0.395(5)	0.670(3)	0.089(4)	0.16(2)
H(162)	0.337(4)	0.637(2)	0.003(3)	0.13(2)
H(18)	0.207(2)	1.003(2)	0.404(2)	0.07(1)
H(19)	0.395(3)	0.965(2)	0.376(2)	0.09(1)
H(20)	0.380(3)	0.863(2)	0.251(2)	0.08(1)
H(21)	-0.001(3)	0.899(2)	0.274(3)	0.09(1)
H(221)	0.009(6)	1.006(4)	0.405(4)	0.22(3)
H(222)	-0.095(5)	0.973(3)	0.369(3)	0.16(2)

TABLE 3 (continued)

1	2	3	4	5
		Molecule **B**		
N(1)	0.3517(2)	1.4072(1)	0.1992(2)	0.0594(7)
C(1)	0.1620(3)	1.1854(2)	0.1312(3)	0.083(1)
C(2)	0.1664(3)	1.1194(3)	0.1659(3)	0.083(1)
C(3)	0.2539(4)	1.0754(2)	0.1492(3)	0.074(1)
C(4)	0.3397(3)	1.0964(2)	0.0955(3)	0.070(1)
C(5)	0.3221(4)	1.1558(2)	0.0444(3)	0.079(1)
C(6)	0.2338(4)	1.1997(2)	0.0618(3)	0.083 (1)
C(7)	0.1022(5)	1.2438(4)	0.1783(6)	0.125(2)
C(8)	0.1762(3)	1.2843(3)	0.2452(4)	0.085(1)
C(9)	0.2938(3)	1.2558(2)	0.2602(2)	0.0553(8)
C(10)	0.3816(2)	1.2787(1)	0.2070(2)	0.0453(7)
C(11)	0.4672(3)	1.2318(2)	0.1907(2)	0.0487(8)
C(12)	0.4685(3)	1.1653(2)	0.2256(2)	0.0555(8)
C(13)	0.3975(3)	1.1514(2)	0.2945(2)	0.068(1)
C(14)	0.3111(3)	1.1963(2)	0.3111(2)	0.067(1)
C(15)	0.5292(4)	1.1067(2)	0.1807(4)	0.079(1)
C(16)	0.4557(4)	1.0662(3)	0.1091(4)	0.096(1)
C(17)	0.3782(2)	1.3448(2)	0.1581(2)	0.0490(7)
C(18)	0.3513(3)	1.4584(2)	0.1345(3)	0.074(1)
C(19)	0.3776(3)	1.4298(2)	0.0549(4)	0.079(1)
C(20)	0.3950(3)	1.3589(2)	0.0697(3)	0.0623(9)
C(21)	0.3359(3)	1.4157(2)	0.2930(3)	0.075(1)
C(22)	0.2816(4)	1.4672(3)	0.3290(5)	0.104(2)
H(2)	0.114(4)	1.108(2)	0.220(3)	0.12(1)
H(3)	0.262(3)	1.032(2)	0.185(2)	0.08(1)
H(5)	0.375(3)	1.168(2)	0.004(2)	0.08(1)
H(6)	0.228(2)	1.243(2)	0.034(2)	0.06(1)
H(71)	0.037(7)	1.232(4)	0.204(5)	0.24(4)
H(72)	0.097(6)	1.278(4)	0.131(4)	0.20(4)
H(81)	0.144(5)	1.287(3)	0.302 (4)	0.17(2)
H(82)	0.173(3)	1.333(2)	0.236(3)	0.10(1)
H(11)	0.522(2)	1.245(1)	0.150(2)	0.049(8)
H(13)	0.403(2)	1.106(2)	0.323(2)	0.07(1)
H(14)	0.258(3)	1.184(1)	0.354(2)	0.066(9)
H(151)	0.550(4)	1.070(2)	0.234(3)	0.13(2)
H(152)	0.584(4)	1.127(2)	0.148(3)	0.12(2)
H(161)	0.497(5)	1.066(3)	0.049(4)	0.18(2)
H(162)	0.452(4)	1.019(2)	0.134(3)	0.12(2)
H(18)	0.344(2)	1.505(2)	0.155(2)	0.06(1)
H(19)	0.386(3)	1.453(2)	-0.000(3)	0.11(1)
H(20)	0.409(3)	1.323(2)	0.024(2)	0.08(1)
H(21)	0.367(3)	1.375(2)	0.333(3)	0.11(1)
H(221)	0.272(4)	1.467(2)	0.393(3)	0.13(2)
H(222)	0.246(3)	1.503(2)	0.287(2)	0.09(1)

The pyrrole fragments of molecules **A** and **B** differ in bond length [$C_{(17)}$–$C_{(20)}$, 1.374(4) and 1.351(5) Å respectively] and the size of the valence angle [$C_{(18)}$–$N_{(1)}$–$C_{(21)}$, 125.4(3) and 126.9(3)° respectively]. It is possible that these differences are caused by the sizes of the dihedral angles between the paracyclophane, pyrrole, and vinyl fragments.

TABLE 4. Bond Lengths (*d*, Å) in Molecules **A** and **B**

Bond	A	B	Bond	A	B
N(1)–C(18)	1.376(4)	1.370(4)	C(9)–C(14)	1.390(4)	1.378(5)
N(1)–C(17)	1.387(4)	1.384(4)	C(9)–C(10)	1.415(4)	1.407(4)
N(1)–C(21)	1.414(4)	1.410(4)	C(10)–C(11)	1.384(4)	1.394(4)
C(1)–C(2)	1.381(6)	1.368(5)	C(10)–C(17)	1.461(4)	1.461(4)
C(1)–C(6)	1.384(5)	1.389(6)	C(11)–C(12)	1.374(4)	1.378(4)
C(1)–C(7)	1.507(6)	1.514(7)	C(12)–C(13)	1.395(5)	1.375(5)
C(2)–C(3)	1.356(6)	1.377(5)	C(12)–C(15)	1.503(5)	1.508(5)
C(3)–C(4)	1.396(6)	1.382(5)	C(13)–C(14)	1.363(5)	1.378(5)
C(4)–C(5)	1.380(5)	1.379(5)	C(15)–C(16)	1.580(7)	1.556(6)
C(4)–C(16)	1.485(6)	1.514(6)	C(17)–C(20)	1.374(4)	1.351(4)
C(5)–C(6)	1.367(5)	1.386(6)	C(18)–C(19)	1.346(5)	1.343(6)
C(7)–C(8)	1.557(6)	1.517(7)	C(19)–C(20)	1.393(5)	1.395(5)
C(8)–C(9)	1.506(4)	1.522(5)	C(21)–C(22)	1.263(6)	1.308(5)

TABLE 5. Valence Angles (ω, deg) in Molecules **A** and **B**

Angle	A	B	Angle	A	B
C(18)–N(1)–C(17)	109.0(3)	108.3(3)	C(11)–C(10)–C(9)	118.0(3)	117.8(3)
C(18)–N(1)–C(21)	125.4(3)	126.9(3)	C(11)–C(10)–C(17)	118.1(3)	119.0(3)
C(17)–N(1)–C(21)	125.2(3)	124.7(3)	C(9)–C(10)–C(17)	123.2(3)	122.6(3)
C(2)–C(1)–C(6)	115.4(5)	116.3(4)	C(12)–C(11)–C(10)	123.2(3)	122.3(3)
C(2)–C(1)–C(7)	121.5(4)	121.9(6)	C(11)–C(12)–C(13)	116.3(3)	117.2(3)
C(6)–C(1)–C(7)	121.8(4)	120.5(6)	C(11)–C(12)–C(15)	121.2(3)	120.1(4)
C(3)–C(2)–C(1)	121.6(4)	121.4(4)	C(13)–C(12)–C(15)	121.2(3)	121.9(3)
C(2)–C(3)–C(4)	121.4(4)	120.8(4)	C(14)–C(13) –C(12)	120.5(3)	120.0(4)
C(5)–C(4)–C(3)	115.6(5)	116.9(4)	C(13) –C(14)–C(9)	121.8(3)	121.5(3)
C(5)–C(4)–C(16)	121.2(5)	120.9(4)	C(12)–C(15)–C(16)	112.7(4)	113.6(3)
C(3)–C(4)–C(16)	121.7(4)	120.7(4)	C(4)–C(16)–C(15)	113.3(4)	113.1(3)
C(6)–C(5)–C(4)	121.0(4)	120.4(4)	C(20) –C(17)–N(1)	106.2(3)	107.1(3)
C(5)–C(6)–C(1)	121.7(4)	121.0(4)	C(20)–C(17)–C(10)	129.2(3)	130.2(3)
C(1)–C(7)–C(8)	112.8(3)	113.7(4)	N(1)–C(17)–C(10)	124.5(3)	122.7(3)
C(9)–C(8)–C(7)	113.7(3)	115.2(4)	C(19)–C(18)–N(1)	108.1(3)	108.5(4)
C(14)–C(9)–C(10)	116.9(3)	117.5(3)	C(18)–C(19)–C(20)	108.1(3)	107.6(4)
C(14)–C(9)–C(8)	119.4(3)	119.8(3)	C(17)–C(20)–C(19)	108.6(3)	108.6(4)
C(10)–C(9)–C(8)	122.3(3)	121.1(3)	C(22)–C(21)–N(1)	125.8(5)	124.9(5)

EXPERIMENTAL

The ^{1}H NMR spectra were recorded for ~2% solutions of compounds in $CDCl_3$ on a Bruker WP 200 (200 MHz) spectrometer, and the ^{13}C NMR spectra for 10% solutions on a Bruker WM 400 (100 MHz) instrument at 30°C. Chemical shifts were measured relative to TMS and to solvent $CDCl_3$ (^{13}C, δ 77.0 ppm) as internal standard. The mass spectra were obtained on MX 1303 and Kratos MS 2 SRF instruments. The IR spectra were recorded on a UR 20 spectrophotometer in KBr disks. Aluminum oxide of Brockmann activity grade II was used for preparative chromatography and plates with a bound layer of aluminum oxide and silica gel of types Alufol and Silufol UV 254 were used for TLC.

X-Ray Structural Analysis of Compound 3. The crystals were monoclinic, space group $P2_{1/C}$: a = 11.997(3), b = 19.222(6), c = 14.721(6) Å; V = 3392(2) Å^3; Z = 8; d_{calc} = 1.172 g/cm^3; μ(MoKα) = 0.067 mm^{-1}. The diffraction experiment was carried out on a Cad-4 diffractometer (MoKα radiation, graphite

monochromator, ω scanning, $2\theta_{max} = 48°$, 3237 reflections with $F^2 \geq 3\sigma(I)$. The structure was solved by the direct method with the SHELXL-93 [16] program to R 0.041 ($wR_2 = 0.098$).

Oxime of 5-Acetyl[2,2]paracyclophane (1). 5-Acetyl[2,2]paracyclophane (10 g, 0.04 mol), hydroxylamine hydrochloride (5.56 g, 0.08 mol), and sodium acetate (9.84 g, 0.12 mol) in 2-propanol (150 ml) were boiled for 3 h (check by TLC). The mixture was cooled, the solid was filtered off, and washed with water. Oxime **1** (9.96 g, 94%) was obtained as colorless crystals of mp 173-175°C (ethyl acetate), R_f 0.53 (Alufol, chloroform–heptane, 1.5:1). IR spectrum, ν, cm^{-1}: 3330 (OH). ^{13}C NMR spectrum (100 MHz, $CDCl_3$), δ, ppm: 157.3 (C=N); 139.6, 139.5, 139.3 ($C_{(5)}$, $C_{(4)}$, $C_{(7)}$); 138.0, 137.6 ($C_{(1)}$, $C_{(10)}$); 135.8 (d, $C_{(6)}$); 133.4, 132.8 (d, $C_{(15)}$, $C_{(16)}$); 132.7, 132.4, 132.3, 131.2 (d, $C_{(11)}$, $C_{(12)}$, $C_{(13)}$, $C_{(14)}$); 35.5, 35.3, 35.2 (t, $C_{(2)}$, $C_{(8)}$, $C_{(9)}$); 34.8 (m, $C_{(3)}$); 15.8 (q, CH_3). Mass spectrum, *m/z* (I_{rel}, %): 265 (30), 248 (3), 161 (35), 160 (32), 144 (100), 143 (20), 142 (5), 128 (5), 115 (13), 105 (20), 104 (28), 103 (19), 91 (10), 78 (16), 77 (18). Found, %: C 80.00; H 7.40; N 5.10. M^+ 265. $C_{18}H_{19}NO$. Calculated, %: C 80.02; H 7.20; N 5.30. M 265.

2-([2,2]-5-Paracyclophanyl)pyrrole (2), 2-([2,2]-5-Paracyclophanyl)-1-vinylpyrrole (3), and 5-(1-Vinyloxyiminoethyl)[2,2]paracyclophane (4). A. Acetylene was bubbled through a solution of oxime **1** (5 g, 19 mmol) and potassium hydroxide (0.11 g, 19 mmol) in DMSO (50 ml) at 95-100°C for 4 h (check by TLC). The mixture was poured onto ice and extracted with ether (5 × 100 ml). The ether extract was dried over magnesium sulfate. After distillation of the solvent the residue (4.7 g) was chromatographed on a column (2.5 × 55 cm) of aluminum oxide, eluent being ethyl acetate–heptane, 1:40. Initially the oxime vinyl ether **4** (0.31 g, 5.6%) was washed off, white crystals mp 86-87°C (ethyl acetate–heptane), R_f 0.75 (silufol, ethyl acetate–heptane, 1:3). Mass spectrum, *m/z* (I_{rel}, %): 291 (25) M^+, 263 (20), 248 (100), 144 (80), 104 (7). Found, %: C 82.61; H 7.22; N 4.99. M^+ 291. $C_{20}H_{21}NO$. Calculated, %: C 82.50; H 7.20; N 4.81. M 291. Then pyrrole **2** (1.14 g, 22%) was washed off as colorless crystals, becoming pink on standing, mp 135-137°C (ethyl acetate–heptane), R_f 0.60 (silufol, ethyl acetate–heptane, 1:3). IR spectrum, ν, cm^{-1}: 3434 (NH). Mass spectrum, *m/z* (I_{rel}, %): 273 (30) M^+, 169 (38), 168 (100), 167 (25), 142 (8), 141 (13), 131 (28), 115 (16), 104 (100), 69 (70). Found, %: C 87.89; H 6.98; N 5.10. M^+ 273. $C_{20}H_{19}N$. Calculated, %: C 87.91; H 6.95; N 5.12. M 273. Finally 5-acetyl[2,2]paracyclophane (0.14 g) was washed off. Colorless crystals, mp 104-105°C (heptane). A mixing test with an authentic sample gave no depression of melting point.

B. The procedure described above using oxime **1** (5 g, 19 mmol) and rubidium hydroxide (0.99 g, 19 mmol) in DMSO (50 ml) at 95-100°C gave compound **2** (0.73 g, 14%), mp 136-137°C (ethyl acetate–heptane), a sample of which gave no depression of melting point in a mixing test with the sample obtained in A; the N-vinyl-substituted pyrrole **3** (0.8 g:14%), colorless crystals, mp 74-76°C (ethyl acetate–heptane), mass spectrum, *m/z* (I_{rel}, %): 299 (100), 195 (40), 194 (90), 180 (22), 168 (6), 167 (10), 152 (8), 141 (6), 128 (6), 104 (8), and 5-acetyl[2,2]paracyclophane (0.33 g), mp 103-104°C.

5-Formyl-2-([2,2]-5-paracyclophanyl)pyrrole (5). Pyrrole **2** (1 g, 3.7 mmol) in DMF (5 ml) was added dropwise to Vilsmeier reagent obtained from DMF (2.7 g, 37 mmol) and freshly distilled phosphorus oxychloride (2.3 g, 14 mmol) at -5°C. The mixture was left at 20°C for 2 h (check by TLC), made alkaline to pH 8 with 10% aqueous sodium carbonate solution, extracted with chloroform (3 × 20 ml), and the extract dried over magnesium sulfate. After distillation of the chloroform the residue (1.42 g) was chromatographed on a column (2.9 × 20 cm) of aluminum oxide, eluting with chloroform. Compound **5** (0.76 g, 69%) was isolated as yellow crystals, mp 152-153°C (ethyl acetate–heptane), R_f 0.67 (silufol, ethyl acetate–heptane, 1:4). IR spectrum, ν, cm^{-1}: 3284 (NH), 1660 (CO). Mass spectrum, *m/z* (I_{rel}, %): 301 (10) M^+, 197 (3), 196 (3), 169 (10), 168 (10), 115 (17), 104 (100), 103 (70), 102 (23), 101 (16), 91 (18), 86 (61), 78 (22). Found, %: C 84.03; H 6.51; N 5.19. M^+ 301. $C_{21}H_{19}NO$. Calculated, %: C 83.70; H 6.31; N 4.65. M 301.

5-Nitro-2-([2,2]-5-paracyclophanyl)pyrrole (6). Compound **2** (0.2 g, 0.73 mmol) in acetic anhydride (5 ml) was added dropwise to a suspension of $Cu(NO_3)_2.3H_2O$ (0.18 g, 0.73 mmol) in acetic anhydride (5 ml) at -12°C. After 1 h (check by TLC) the reaction mixture was treated with saturated sodium carbonate solution to pH 8, and extracted with ether (4 × 20 ml). The extract was dried over magnesium sulfate. After distillation of

ether the residue (0.18 g) was chromatographed on a column (3.2 × 19 cm) of aluminum oxide, eluting with ethyl acetate–heptane. Pyrrole **6** (80 mg, 34.5%) was obtained as yellow crystals, mp 168-170°C (ethyl acetate–heptane), R_f 0.79 (Silufol, ethyl acetate–heptane, 1:4). IR spectrum, ν, cm^{-1}: 1570 and 1360 (NO_2). Mass spectrum, *m/z* (I_{rel}, %): 318 (8) $[M]^+$, 288 (2), 272 (46), 214 (4), 197 (15), 168 (31), 167 (23), 166 (15), 149 (15), 146 (23), 145 (11), 144 (11), 141 (15), 115 (19), 105 (38), 104 (100), 91 (50). Found, %: C 75.83; H 5.32; N 9.05. M^+ 318. $C_{20}H_{18}N_2O_2$.. Calculated, %: C 75.47; H 5.66; N 8.81. M 318.

1-(β-Cyanoethyl)-5-formyl-2-([2,2]-5-paracyclophanyl)pyrrole (7). A solution of formylpyrrole **5** (0.3 g, 0.99 mmol) and acrylonitrile (0.053 g, 1.9 mmol) in absolute benzene (25 ml) was heated at 65°C for 5 h in a current of nitrogen in the presence of Triton B (5 drops) (check by TLC). The benzene was distilled off, water (10 ml) was added, the mixture was extracted with chloroform, and the extract dried over magnesium sulfate. After distilling off the chloroform the residue (0.43 g) was purified on a column (2.9 × 22 cm) of aluminum oxide, eluent being chloroform. Compound **7** (0.26 g, 65%) was obtained as pink crystals of mp 166-168°C, R_f 0.51 (Silufol, ethyl acetate–heptane, 1:4). IR spectrum, ν, cm^{-1}: 2260 (CN), 1660 (CO). Mass spectrum, *m/z* (I_{rel}, %): 354 (31) M^+, 314 (5), 250 (13), 249 (17), 222 (35), 221 (32), 182 (20), 181 (31), 180 (27), 168 (19), 167 (25), 166 (16), 149 (40), 105 (100), 104 (100), 91 (43). Found, %: C 81.53; H 5.87; N 8.05. M^+ 354. $C_{24}H_{22}N_2O$. Calculated, %: C 81.36; H 6.21; N 7.91. M 354.

2-Formyl-5-([2,2]-5-paracyclophanyl)-3H-pyrrolizine (8). A solution of formylpyrrole **5** (0.3 g, 0.99 mmol) and acrolein (0.12 g, 1.9 mmol) in absolute benzene (25 ml) was heated at 50°C for 1.5 h in a current of nitrogen in the presence of Triton B (5 drops) (check by TLC). The benzene was distilled off, water (10 ml) was added, the mixture was extracted with chloroform, and the extract dried over magnesium sulfate. After distilling off the chloroform the residue (0.32 g) was purified on a column (1.2 × 40 cm) of aluminum oxide, eluting with ethyl acetate–heptane, 1:10. Pyrrolizine **8** (40 mg, 36%) was isolated as yellow crystals of mp 128-129°C (ethyl acetate–heptane), R_f 0.67 (Silufol, ethyl acetate–heptane, 1:4). IR spectrum, ν, cm^{-1}: 1770 (CO). Mass spectrum, *m/z* (I_{rel}, %): 339 (3) M^+, 338 (8), 310 (5), 235 (4), 206 (7), 169 (16), 168 (15), 167 (58), 105 (42), 104 (31), 97 (100), 91 (31). Found, %: C 85.10; H 6.51; N 3.92. M^+ 339. $C_{24}H_{21}NO$. Calculated, %: C 84.96; H 6.19; N 4.13. M 339.

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