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CONCERNING THE PRODUCT OF [2 + 2] CYCLODIMERIZATION OF 9-ALLENYLCARBAZOLE

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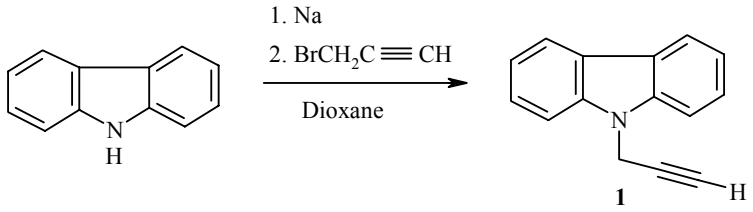
The isomerization of 9-propargylcarbazole in alcoholic alkali leads to the product of dimerization of 9-allenylcarbazole, 1,2-bis(9-carbazolylmethylene)cyclobutane, the structure of which was established by X-ray diffraction analysis.

Keywords: allenylcarbazole, 1,2-bis(9-carbazolylmethylene)cyclobutane, cyclodimerization.

We have synthesized 9-propargylcarbazole **1** with the aim of studying its properties and application in synthesis of acetylene derivatives of carbazole. This was achieved by the action of propargyl bromide on carbazolylsodium, prepared in 80% yield by heating metallic sodium and carbazole in dioxane. This compound was obtained previously by the action of propargyl bromide on the sodium derivative of carbazole in liquid ammonia [1,2], in DMF [3], or in acetonitrile [4]. The patented procedure [5] differed in the use of potassium derivative of carbazole.



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Both on carrying out the synthesis and on studying the Favorsky rearrangement of 9-propargylcarbazole **1** (heating in alcoholic alkali) we noted the formation of a difficultly soluble product, which became predominant on boiling compound **1** in alcoholic KOH solution for 8 h. The formation of difficultly soluble solid on rearranging compound **1** has been observed previously. For example, the authors of [1], while studying the isomerization of N-propargyl-substituted heterocycles, assumed it to be a polymer. We have established that under the conditions indicated above the main product of isomerization of carbazole **1** is an individual compound having the same elemental composition as the initial carbazole **1**. The structures of the isomeric 9-allenylcarbazole **2** and 9-propynylcarbazole **3** are excluded according to the spectral characteristics, by the

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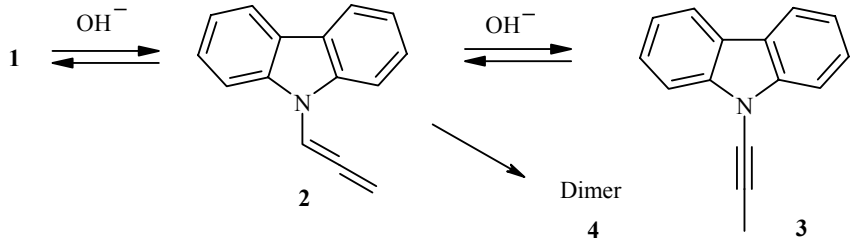
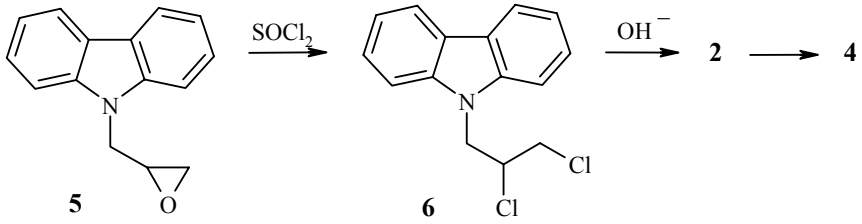
lack of carbonyl group absorption band, and also of allenic and acetylenic bonds (at 1950-1980 and 2100-2200 cm^{-1}) and by the presence in the ^1H NMR spectrum of a complete set of signals for the aromatic protons of carbazole nucleus substituted at position 9.

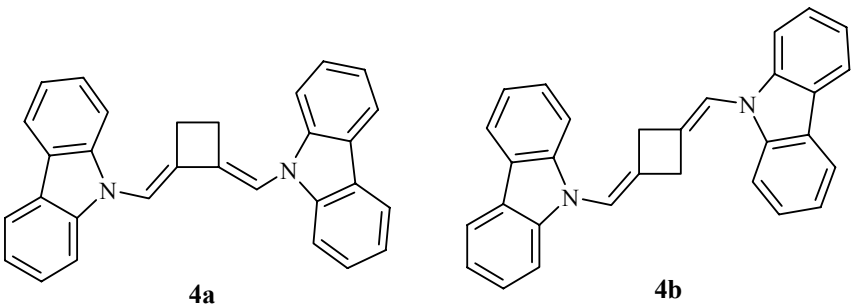


The compound obtained is neither an oxidation product of propargylcarbazole **1,** nor the hydrolysis product of allene **2**, nor the cyclization product of the latter into a derivative of pyrrolocarbazole, which might have been expected on the basis of the results of [6]. The molecular weight measured by the Rast method, proving to be double the molecular weight of the initial compound **1**, enabled the dimeric structure to be proposed, i.e. bis(9-carbazolylmethylene)cyclobutane (**4**), the product of [2 + 2] cyclodimerization of 9-allenylcarbazole **2**. The significant predominance of allene **2** in the equilibrium mixture compared with the other isomers **1** and **3**, recorded by the authors of [1] on carrying out the isomerization using alkaline catalysts, also points in favor of allene dimer. According to the data of the same authors, this special feature is probably most widely expressed among carbazole derivatives. On isomerizing propargylcarbazole under certain other conditions (potassium hydroxide in DMSO at room temperature) used by the authors of [3,7], 9-allenylcarbazole **2** was isolated in almost quantitative yield.

We have shown that in the simpler and more convenient way dimer **4** may be obtained from the available [8] epoxypropylcarbazole **5**, as shown in the Scheme.



The dimerization of allenes [8] may lead to 1,2- and 1,3-disubstituted derivatives of cyclobutane, and on the basis of the data obtained it is not possible to make an unequivocal choice between the structures of 1,2- and 1,3-bis(9-carbazolylmethylene)cyclobutane (**4a** and **4b** respectively). We therefore carried out an X-ray diffraction investigation of the dimerization product **4**, showing unequivocally that the obtained dimer corresponds to structure **4a** (Fig. 1, Tables 1-3).



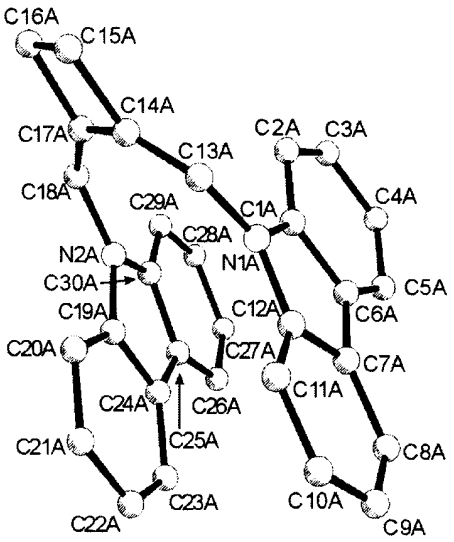


Fig. 1. Structure of 1,2-bis(9-carbazolylmethylene)cyclobutane **4a** molecule.

TABLE 1. Coordinates ($\times 10^4$) and Equivalent Isotropic Thermal Parameters ($\times 10^3$) of the Non-hydrogen Atoms in the Structure of Compound **4a**

Atom	*x*	*y*	*z*	U_{eq}, Å^2
1	2	3	4	5
N(1A)	6189(7)	3687(2)	9927(5)	40(1)
N(2A)	6316(7)	4418(2)	12725(6)	39(1)
C(1A)	7760(9)	3805(3)	10852(8)	39(2)
C(2A)	8749(9)	3595(3)	12177(7)	44(2)
C(3A)	10327(10)	3768(3)	12885(7)	60(2)
C(4A)	11011(10)	4138(3)	12277(9)	67(2)
C(5A)	10005(10)	4339(3)	10955(9)	58(2)
C(6A)	8438(10)	4176(3)	10223(7)	44(2)
C(7A)	7153(9)	4278(3)	8810(7)	49(2)
C(8A)	7005(10)	4599(3)	7662(8)	56(2)
C(9A)	5602(11)	4598(3)	6447(7)	61(2)
C(10A)	4294(10)	4284(3)	6327(7)	65(2)
C(11A)	4405(9)	3961(3)	7430(7)	52(2)
C(12A)	5794(10)	3961(3)	8650(7)	42(2)
C(13A)	5171(8)	3325(2)	10146(7)	46(2)
C(14A)	4883(8)	3272(2)	11310(6)	43(2)
C(15A)	4068(9)	2835(3)	11721(7)	58(2)
C(16A)	4669(9)	3072(2)	13224(7)	55(2)
C(17A)	5336(8)	3525(2)	12706(6)	40(2)
C(18A)	5936(8)	3976(3)	13342(6)	48(2)
C(19A)	5285(10)	4642(3)	11373(8)	41(2)
C(20A)	3762(10)	4497(3)	10422(7)	45(2)
C(21A)	3017(9)	4800(3)	9201(7)	53(2)
C(22A)	3846(10)	5218(3)	8931(7)	57(2)
C(23A)	5355(10)	5355(3)	9900(7)	52(2)
C(24A)	6140(9)	5063(2)	11153(7)	42(2)

TABLE 1 (continued)

1	2	3	4	5
C(25A)	7637(10)	5119(3)	12417(7)	46(2)
C(26A)	8972(9)	5468(3)	12819(7)	55(2)
C(27A)	10253(11)	5415(3)	14141(9)	70(3)
C(28A)	10239(10)	5021(3)	15083(8)	71(2)
C(29A)	8982(10)	4668(3)	14672(8)	55(2)
C(30A)	7683(9)	4724(2)	13367(7)	38(2)
N(1B)	8176(7)	2540(2)	9548(6)	41(2)
N(2B)	8080(6)	1833(2)	6736(5)	39(1)
C(1B)	8564(9)	2265(2)	10826(6)	42(2)
C(2B)	9974(10)	2256(3)	12073(8)	53(2)
C(3B)	10034(10)	1942(3)	13180(7)	60(2)
C(4B)	8718(13)	1633(3)	13036(8)	67(2)
C(5B)	7307(10)	1644(3)	11803(8)	58(2)
C(6B)	7211(9)	1965(3)	10666(7)	42(2)
C(7B)	5961(10)	2066(3)	9249(8)	45(2)
C(8B)	4364(10)	1900(3)	8540(8)	55(2)
C(9B)	3392(9)	2114(3)	7204(8)	65(2)
C(10B)	4052(10)	2483(3)	6605(8)	60(2)
C(11B)	5613(10)	2655(3)	7264(7)	51(2)
C(12B)	6591(10)	2426(2)	8595(7)	37(2)
C(13B)	9235(7)	2908(2)	9364(6)	40(2)
C(14B)	9489(7)	2967(2)	8191(6)	41(2)
C(15B)	10365(9)	3416(3)	7825(7)	58(2)
C(16B)	9761(9)	3184(3)	6287(7)	59(2)
C(17B)	9055(8)	2719(2)	6793(6)	44(2)
C(18B)	8460(8)	2274(2)	6130(6)	44(2)
C(19B)	6688(10)	1536(3)	6086(8)	47(2)
C(20B)	5366(9)	1605(3)	4760(8)	51(2)
C(21B)	4090(10)	1257(3)	4394(8)	70(2)
C(22B)	4086(11)	863(3)	5310(9)	72(2)
C(23B)	5405(11)	795(3)	6604(9)	61(2)
C(24B)	6712(9)	1126(2)	7014(7)	42(2)
C(25B)	8216(9)	1167(3)	8266(7)	43(2)
C(26B)	9014(11)	877(3)	9514(8)	56(2)
C(27B)	10547(13)	1010(3)	10487(9)	67(3)
C(28B)	11397(9)	1437(3)	10262(7)	57(2)
C(29B)	10620(10)	1736(3)	9045(7)	45(2)
C(30B)	9090(10)	1609(3)	8066(7)	40(2)

This variant of the dimerization of 9-allenylcarbazole **2** is effected in our opinion as a result of the association of the heterocyclic fragments in solution with the formation of eximers (resonance interaction).

There are two molecules (**A** and **B**) in the symmetrically independent part of the unit cell. The molecule of compound **4a** has a conformation in which the two π-electron systems are disposed practically parallel one above the other (the angle between them is 12.9° in molecule **A** and 12.4° in molecule **B**). The conjugated cyclic systems are not entirely planar, the angle between the planes of the benzene rings is 4.2 and 5.1° in **A** and 5.1 and 3.6° in **B**. The cyclobutane ring is bent somewhat along the C(15)–C(17) bond (the angle between the planes of C(14), C(15), C(17) and C(15), C(16), C(17) is 6.7° in conformer **A** and 7.3° in conformer **B**). The exocyclic double bonds C(13)–C(14) and C(18)–C(17) are twisted somewhat relative to one another [torsion angle C(13)–C(14)–C(17)–C(18) is 19(2) in **A** and -16(2)° in **B**]. The conjugation between the tricyclic

fragments and the double bonds is disturbed to a significant extent as a result of their noncoplanarity [torsion angle C(1)–N(1)–C(13)–C(14) is 48.1(9) in **A**, 139.9(7)° in **B** and C(19)–N(2)–C(18)–C(17) is 47.0(9) in **A**, 136.3(7)° in **B**].

Such a conformation of the molecule is probably caused by significant steric stress as shown by shortened intramolecular contacts for H(2A)–C(14A) at 2.84 (sum of van der Waals radii 2.87 [11]), H(2A)–C(17A) 2.82 (2.87), H(11A)–C(13A) 2.84 (2.87), H(20A)–C(14A) 2.75 (2.87), H(20A)–C(17A) 2.81 (2.87), C(20A)–C(12A) 3.38 (3.42), C(20A)–C(13A) 3.32 (3.42), C(20A)–C(14A) 3.31 (3.42), C(20A)–C(17A) 3.31 (3.42), N(2A)–C(1A) 3.17 (3.21), C(19A)–N(1A) 3.15 (3.21), C(19A)–C(1A) 3.30 (3.42), C(21A)–C(11A) 3.39 (3.42), C(18A)–C(2A) 3.38 (3.42), H(11B)–C(14B) 2.85 (2.87), H(11B)–C(17B) 2.82 (2.87), H(29B)–C(14B) 2.77 (2.87), H(29B)–C(17B) 2.82 Å (2.87 Å).

TABLE 2. Bond Lengths (*l*) in the Structure of Compound **4a**

Bond	*l*, Å	Bond	*l*, Å
N(1A)–C(1A)	1.367(8)	N(1A)–C(13A)	1.390(8)
N(1A)–C(12A)	1.396(8)	N(2A)–C(30A)	1.374(8)
N(2A)–C(18A)	1.411(8)	N(2A)–C(19A)	1.426(8)
C(1A)–C(2A)	1.384(9)	C(1A)–C(6A)	1.427(9)
C(2A)–C(3A)	1.371(9)	C(3A)–C(4A)	1.41(1)
C(4A)–C(5A)	1.38(1)	C(5A)–C(6A)	1.357(9)
C(6A)–C(7A)	1.449(9)	C(7A)–C(8A)	1.398(9)
C(7A)–C(12A)	1.42(1)	C(8A)–C(9A)	1.352(9)
C(9A)–C(10A)	1.39(1)	C(10A)–C(11A)	1.373(9)
C(11A)–C(12A)	1.348(8)	C(13A)–C(14A)	1.336(8)
C(14A)–C(17A)	1.469(8)	C(14A)–C(15A)	1.495(8)
C(15A)–C(16A)	1.530(8)	C(16A)–C(17A)	1.507(8)
C(17A)–C(18A)	1.325(8)	C(19A)–C(20A)	1.359(8)
C(19A)–C(24A)	1.402(9)	C(20A)–C(21A)	1.385(9)
C(21A)–C(22A)	1.401(9)	C(22A)–C(23A)	1.351(9)
C(23A)–C(24A)	1.396(9)	C(24A)–C(25A)	1.432(8)
C(25A)–C(30A)	1.396(9)	C(25A)–C(26A)	1.42(1)
C(26A)–C(27A)	1.369(9)	C(27A)–C(28A)	1.40(1)
C(28A)–C(29A)	1.37(1)	C(29A)–C(30A)	1.365(9)
N(1B)–C(12B)	1.381(8)	N(1B)–C(1B)	1.399(8)
N(1B)–C(13B)	1.413(8)	N(2B)–C(19B)	1.377(9)
N(2B)–C(18B)	1.403(8)	N(2B)–C(30B)	1.407(8)
C(1B)–C(2B)	1.373(8)	C(1B)–C(6B)	1.39(1)
C(2B)–C(3B)	1.38(1)	C(3B)–C(4B)	1.38(1)
C(4B)–C(5B)	1.365(9)	C(5B)–C(6B)	1.403(9)
C(6B)–C(7B)	1.439(9)	C(7B)–C(8B)	1.380(9)
C(7B)–C(12B)	1.398(9)	C(8B)–C(9B)	1.39(1)
C(9B)–C(10B)	1.39(1)	C(10B)–C(11B)	1.353(9)
C(11B)–C(12B)	1.405(9)	C(13B)–C(14B)	1.329(8)
C(14B)–C(17B)	1.466(8)	C(14B)–C(15B)	1.532(8)
C(15B)–C(16B)	1.557(9)	C(16B)–C(17B)	1.544(9)
C(17B)–C(18B)	1.320(8)	C(19B)–C(20B)	1.392(9)
C(19B)–C(24B)	1.414(9)	C(20B)–C(21B)	1.38(1)
C(21B)–C(22B)	1.38(1)	C(22B)–C(23B)	1.37(1)
C(23B)–C(24B)	1.37(1)	C(24B)–C(25B)	1.426(8)
C(25B)–C(26B)	1.393(9)	C(25B)–C(30B)	1.443(9)
C(26B) –C(27B)	1.36(1)	C(27B)–C(28B)	1.41(1)
C(28B)–C(29B)	1.379(9)	C(29B)–C(30B)	1.361(9)

This leads to a lengthening of bonds N(1)–C(13) 1.390(8) (**A**), 1.413(8) (**B**), and N(2)–C(18) 1.411(8) (**A**), 1.403(68) Å (**B**) compared with the mean value of 1.355 Å [10].

Such a sterically stressed conformation of the molecule is probably stabilized to a significant degree by fairly strong stacking interactions between the π-systems of the tricyclic fragments. Their close-to-parallel orientation and the distances between the fragment atoms being in the range 3.15 to 3.8 Å indicates this.

The compound **4a** molecules in the crystal form mutually perpendicular stacks along the crystallographic directions (1 0 0) and (0 0 1). The angle between the planes of the tricyclic fragments of neighboring molecules (0.7°) and the distance between the spatially adjacent π-systems (3.55 Å) suggests the presence of intermolecular stacking interactions also. Shortened intermolecular contacts were detected in the crystal between molecules located in the independent part of the unit cell, H(13A)–C(12B) 2.83 (*x*, *y*, *z*) and H(13B)–C(1A) 2.85 Å (*x*, *y*, *z*).

The presence in the crystal structure of compound **4a** of intra- and intermolecular stacking interactions creates conditions for carrying out various topochemical reactions, which may lead to both intra- and intermolecular cyclization involving the tricyclic fragments.

TABLE 3. Bond Angles (ω) in the Structure of Compound **4a**

Angle	ω, deg.	Angle	ω, deg.
1	2	3	4
C(1A)–N(1A)–C(13A)	126.7(5)	C(1A)–N(1A)–C(12A)	108.6(6)
C(13A)–N(1A)–C(12A)	124.5(6)	C(30A)–N(2A)–C(18A)	125.7(6)
C(30A)–N(2A)–C(19A)	108.7(6)	C(18A)–N(2A)–C(19A)	125.4(6)
N(1A)–C(1A)–C(2A)	130.3(7)	N(1A)–C(1A)–C(6A)	110.5(6)
C(2A)–C(1A)–C(6A)	119.0(7)	C(3A)–C(2A)–C(1A)	119.2(8)
C(2A)–C(3A) –C(4A)	122.2(7)	C(5A)–C(4A)–C(3A)	117.4(8)
C(6A)–C(5A)–C(4A)	122(1)	C(5A)–C(6A)–C(1A)	120.1(7)
C(5A)–C(6A)–C(7A)	134.7(8)	C(1A)–C(6A)–C(7A)	105.1(6)
C(8A)–C(7A)–C(12A)	118.0(7)	C(8A)–C(7A)–C(6A)	134.7(8)
C(12A)–C(7A)–C(6A)	107.3(6)	C(9A)–C(8A)–C(7A)	119.8(7)
C(8A)–C(9A)–C(10A)	120.7(6)	C(11A)–C(10A)–C(9A)	120.9(7)
C(12A)–C(11A)–C(10A)	118.9(7)	C(11A)–C(12A)–N(1A)	129.9(7)
C(11A)–C(12A) –C(7A)	121.6(6)	N(1A)–C(12A)–C(7A)	108.4(6)
C(14A)–C(13A)–N(1A)	127.4(6)	C(13A)–C(14A)–C(17A)	138.8(6)
C(13A)–C(14A)–C(15A)	129.5(6)	C(17A)–C(14A)–C(15A)	91.2(5)
C(14A)–C(15A)–C(16A)	89.1(5)	C(17A)–C(16A)–C(15A)	88.4(5)
C(18A)–C(17A)–C(14A)	139.0(6)	C(18A)–C(17A)–C(16A)	129.8(5)
C(14A)–C(17A)–C(16A)	91.0(5)	C(17A)–C(18A)–N(2A)	127.2(5)
C(20A)–C(19A)–C(24A)	123.6(7)	C(20A)–C(19A)–N(2A)	129.5(7)
C(24A)–C(19A)–N(2A)	107.0(6)	C(19A)–C(20A)–C(21A)	117.0(7)
C(20A)–C(21A)–C(22A)	120.9(7)	C(23A)–C(22A)–C(21A)	120.7(6)
C(22A)–C(23A)–C(24A)	120.0(7)	C(23A)–C(24A)–C(19A)	117.7(7)
C(23A)–C(24A)–C(25A)	134.4(7)	C(19A)–C(24A)–C(25A)	107.6(6)
C(30A)–C(25A)–C(26A)	119.1(7)	C(30A)–C(25A)–C(24A)	107.5(6)
C(26A)–C(25A)–C(24A)	133.4(7)	C(27A)–C(26A)–C(25A)	118.9(7)
C(26A)–C(27A)–C(28A)	120.4(7)	C(29A)–C(28A)–C(27A)	120.7(7)
C(30A)–C(29A)–C(28A)	119.2(7)	C(29A)–C(30A)–N(2A)	129.5(7)
C(29A)–C(30A)–C(25A)	121.5(7)	N(2A)–C(30A)–C(25A)	108.9(6)
C(12B)–N(1B)–C(1B)	109.4(6)	C(12B)–N(1B)–C(13B)	127.1(5)
C(1B)–N(1B)–C(13B)	123.3(6)	C(19B)–N(2B)–C(18B)	125.1(6)
C(19B)–N(2B)–C(30B)	109.2(7)	C(18B)–N(2B)–C(30B)	125.7(6)
C(2B)–C(1B)–C(6B)	121.4(6)	C(2B)–C(1B)–N(1B)	130.5(7)

TABLE 3 (continued)

1	2	3	4
C(6B)–C(1B)–N(1B)	108.0(6)	C(1B)–C(2B)–C(3B)	118.6(7)
C(2B)–C(3B)–C(4B)	121.1(7)	C(5B)–C(4B)–C(3B)	120.6(7)
C(4B)–C(5B)–C(6B)	119.4(7)	C(1B)–C(6B)–C(5B)	119.0(7)
C(1B)–C(6B)–C(7B)	107.0(6)	C(5B)–C(6B)–C(7B)	134.0(7)
C(8B)–C(7B)–C(12B)	119.8(7)	C(8B)–C(7B)–C(6B)	132.5(7)
C(12B)–C(7B)–C(6B)	107.5(6)	C(7B)–C(8B)–C(9B)	118.7(8)
C(8B)–C(9B)–C(10B)	119.7(7)	C(11B)–C(10B)–C(9B)	123.3(7)
C(10B)–C(11B)–C(12B)	116.4(8)	N(1B)–C(12B)–C(7B)	108.0(6)
N(1B)–C(12B)–C(11B)	129.7(7)	C(7B)–C(12B)–C(11B)	121.9(7)
C(14B)–C(13B)–N(1B)	125.9(5)	C(13B)–C(14B)–C(17B)	139.8(6)
C(13B)–C(14B)–C(15B)	128.0(6)	C(17B)–C(14B)–C(15B)	92.1(5)
C(14B)–C(15B)–C(16B)	88.1(5)	C(17B)–C(16B)–C(15B)	88.3(5)
C(18B)–C(17B)–C(14B)	139.7(6)	C(18B)–C(17B) –C(16B)	129.0(5)
C(14B)–C(17B)–C(16B)	91.0(5)	C(17B)–C(18B)–N(2B)	126.1(5)
N(2B)–C(19B)–C(20B)	129.3(7)	N(2B)–C(19B)–C(24B)	109.5(6)
C(20B)–C(19B)–C(24B)	121.2(7)	C(21B)–C(20B)–C(19B)	117.1(7)
C(20B)–C(21B)–C(22B)	122.0(7)	C(23B)–C(22B)–C(21B)	120.2(7)
C(24B)–C(23B)–C(22B)	120.1(8)	C(23B)–C(24B)–C(19B)	119.3(7)
C(23B)–C(24B)–C(25B)	133.8(7)	C(19B)–C(24B)–C(25B)	106.9(6)
C(26B)–C(25B)–C(24B)	135.7(7)	C(26B)–C(25B)–C(30B)	116.8(7)
C(24B)–C(25B)–C(30B)	107.4(6)	C(27B)–C(26B)–C(25B)	120.7(8)
C(26B)–C(27B)–C(28B)	121.8(7)	C(29B)–C(28B)–C(27B)	118.5(8)
C(30B)–C(29B)–C(28B)	120.3(8)	C(29B)–C(30B)–N(2B)	131.2(7)
C(29B)–C(30B)–C(25B)	121.9(6)	N(2B)–C(30B)–C(25B)	106.9(6)

EXPERIMENTAL

The ^{1}H NMR spectra were recorded on a Gemini 200 (200 MHz) instrument, internal standard was TMS. The IR spectra were taken on a Specord IR 75 instrument in KBr disks. The numbering of the carbon atoms in the compound **4a** molecule is given in Fig. 1.

X-Ray Diffraction Investigation of Compound 4a. The crystals of compound **4a** are monoclinic, $C_{30}H_{22}N_2$, at 20°C: a = 9.036(2), b = 25,645(7), c = 10.291(2) Å; β = 115.10(2)°; V = 2159.5(9) Å^3; M_r = 410.50; Z = 4; space group $P2_1$; d_{calc} = 1.263 g/cm^3; μ(MoKα) = 0.074 mm^{-1}; F(000) = 864. The parameters of the unit cell and the intensities of 4034 reflections (3795 independent, R_{int} = 0.04) were measured on a Siemens automatic P3/PC four-circle diffractometer (MoK_α, graphite monochromator, 2θ/θ scanning, $2\theta_{max}$ = 50°).

The structure was solved by the direct method with the SHELX97 [12] set of programs. The positions of the hydrogen atoms were clarified by an electron density difference synthesis and refined with a rider model with U_{iso} = 1.2 U_{eq}. The structure was refined according to F^2 by a full-matrix least-squares method with an anisotropic approach for the nonhydrogen atoms to wR_2 = 0.134 for 3795 reflections (R_1 = 0.049 for 1998 reflections with $F > 4\sigma(F)$, S = 0.894). The final coordinates of atoms are given in Table 1, and values of bond lengths and bond angles in Tables 2 and 3.

9-Propargylcarbazole (1). Mixture of carbazole (16.7 g, 0.1 mol) and metallic sodium (2.3 g, 0.1 mol) in anhydrous dioxane (50 ml) was boiled with stirring until complete dissolution of sodium. Propargyl bromide (46.7 g, 0.4 mol) was added with stirring to the boiling mixture. At the end of the intense exothermic reaction the mixture was boiled for a further 15 min, and poured into cold water (500 ml). The separated oil was removed, washed several times with warm water, and left for ~16 h at room temperature. The separated crystals

were filtered off, washed with water, dried, and recrystallized from cyclohexane. Yield 16.4 g (80%); mp 101-102°C. After recrystallization from methanol the compound had mp 106-107°C (mp 108°C [1]).

9-(2,3-Dichloro-1-propyl)carbazole (6). Mixture of 9-epoxypropylcarbazole **5** (22.3 g, 0.1 mol), benzene (50 ml), DMF (0.5 ml), and $SOCl_2$ (12 ml) was heated under reflux on a water bath. After the exothermic reaction had passed the solvent was distilled off, and the residue was recrystallized from cyclohexane. Yield 25 g (90%); mp 90-92°C. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm (*J*, Hz): 4.0 (2H, d, *J* ~ 3.9, N-CH_2); 4.6-4.9 (3H, m, CH and CH_2); 7.2 (2H, t, *J* ~ 7.9, H-2,7); 7.4 (2H, t, *J* ~ 8.0, H-3,6); 7.6 (2H, d, *J* ~ 7.9, H-1,8); 8.1 (2H, d, *J* ~ 8.0, H-4,5). Found, %: C 64.5; H 4.9; Cl 25.6; N 5.2. $C_{15}H_{13}Cl_2N$. Calculated, %: C 64.77; H 4.71; Cl 25.49; N 5.04.

1,2-Bis(9-carbazolylmethylene)cyclobutane (4a). A. Mixture of 9-propargylcarbazole **1** (1.93 g, 0.01 mol), ethanol (5 ml), and KOH (0.1 g) was boiled in nitrogen atmosphere for 8 h. The precipitated solid was filtered off, washed with acetone, and with water, dried in the air, and crystallized from pyridine. Yield 1.5 g (78%) of pale yellow prisms; mp 224-225°C. IR spectrum (KBr), ν, cm^{-1}: 3040, 2960, 2910, 1640, 1620, 1590, 1450, 740, 715. ^{1}H NMR spectrum (Py-d_5), δ, ppm (*J*, Hz): 2.85 (4H, s, 2H-15, 2H-16); 6.54 (2H, s, H-13,18); 6.85 (4H, t, *J* ~ 7.5, H-3,10,21,28); 6.9 (4H, d, *J* ~ 8.1, H-2,11,20,29); 7.1 (4H, t, *J* ~ 7.5, H-4,9,22,27); 7.35 (4H, d, *J* ~ 7.8, H-5,8,23,26). Found, %: C 87.6; H 5.5; N 6.9. $C_{30}H_{22}N_2$. Calculated, %: C 87.77, H 5.40; N 6.82.

B. Mixture of compound **6** (27.8 g, 0.1 mol) and KOH (22.4 g, 0.4 mol) in 2-propanol (50 ml) was boiled with stirring for 24 h. After cooling, the solid was filtered off, washed with acetone, and with water, dried, and crystallized from pyridine. Product **4a** was obtained (9.4 g, 46%); mp 224-225°C. A mixing test with a sample obtained by method A gave no depression of melting point.

REFERENCES

1. A. J. Hubert and H. Reimlinger, *J. Chem. Soc. C*, 606 (1968).
2. J-.L. Dumont, *Compt. Rend.*, **261**, 1710 (1965).
3. J-.L. Dumont, W. Chodkievicz, and P. Cadiot, *Bull. Soc. Chim. Fr.*, 1197 (1967).
4. S. M. Fomin, A. N. Flerova, G. N. Gerasimov, and E. N. Teleshov, USSR Inventor's Certificate 1384578; *Byull. Izobret.*, No. 12, 78 (1988).
5. K. C. Yee, US Patent 4125534; *Chem. Abstr.*, **90**, 88046 (1979).
6. J. Reisch and R. Salchi-Artimani, *Monatsh. Chem.*, **116**, 1099 (1985).
7. G. Broggini, L. Bruche, and G. Zecchi, *J. Chem. Soc., Perkin Trans. 1*, 533 (1990).
8. I. P. Zherebtsov, N. M. Rovkina, V. P. Lopatinskii, and T. P. Katerinich, USSR Inventor's Certificate 486014; *Byull. Izobret.*, No. 36, 62 (1975).
9. H. F. Schuster and G. M. Coppola, in *Allenes in Organic Synthesis*, Wiley, New York (1984), p. 317.
10. H-.B. Burgi and J. D. Dunitz, in *Structure Correlation,* Vol. 2, VCH, Weinheim (1994), p. 741.
11. Yu. V. Zefirov and Yu. V. Zorkii, *Usp. Khim.*, **58**, 713 (1989).
12. G. M. Sheldrick, *SHELX97. PC Version. A System of Computer Programs for Crystal Structure Solution and Refinement, Rev. 2* (1998).