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Stable Carbenes. Synthesis and Properties of Benzimidazol-2-ylidenes

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Abstract—A new stable crystalline carbene, 1,3-bis(1-adamantyl)benzimidazol-2-ylidene, was synthesized by decomposition of 1,3-bis(1-adamantyl)-2,3-dihydro-1*H*-benzimidazol-2-ylacetonitrile on heating under reduced pressure. Heteroaromatic 1,3-R_2-disubstituted benzimidazol-2-ylidenes, both stable (R = 1-Ad) and generated *in situ* (R = Me, Bzl), as well as 1,3,4,5-tetraphenylimidazol-2-ylidene (generated *in situ*), reacted with acetonitrile to give the corresponding insertion products, 1,3-disubstituted 2-cyanomethyl-2,3-dihidro-1*H*-(benz)-imidazoles. The geometric parameters of 1,3-bis(1-adamantyl)benzimidazol-2-ylidene, determined by X-ray analysis, suggest its lower aromaticity as compared to imidazol-2-ylidenes and 1,2,4-triazol-5-ylidenes. The structures of 2-cyanomethyl-2,3-dihydro-1*H*-benzimidazoles, 2-cyanomethyl-1,3,4,5-tetraphenyl-2,3-dihydro-1*H*-imidazole, and 1-(1-adamantyl)-5-cyanomethyl-3,4-diphenyl-4,5-dihydro-1*H*-1,2,4-triazole are characterized by partial conjugation in the heteroring; some compounds exhibit luminescence under UV irradiation. 1,3-Bis(1-adamantyl)benzimidazol-2-ylidene reacted with molecular sulfur in benzene to give 1,3-bis-(1-adamantyl)-2,3-dihydro-1*H*-benzimidazole-2-thione, but it failed to react with selenium under analogous conditions.

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A long and important period including experiments with carbenes generated *in situ* [1, 2] has come to the end when the first stable nucleophilic carbene, 1,3-bis-(1-adamantyl)imidazol-2-ylidene, has been isolated [3]. It was synthesized by deprotonation of 1,3-bis(1-adamantyl)imidazolium chloride with sodium or potassium hydride in the presence of *t*-BuOK or dimsyl anion [4]. Following analogous approaches, several research teams later synthesized new stable heteroaromatic carbenes of the triazole [5] and some other series [6]. The procedures were based on deprotonation of the corresponding azolium salts by the action of such bases as lithium diisopropylamide [7], butyllithium [8], and potassium hexamethyldisilylamide [9]. Hermann et al. [10] succeeded in effecting deprotonation of imidazolium salts with sodium hydride at a relatively low temperature using the system liquid ammonia–tetrahydrofuran as solvent. Stable 1,3,4-triphenyl-4,5-dihydro-1*H*-1,2,4-triazol-5-ylidene was obtained by decomposition of intermediate 5-methoxy-4,5-dihydro-1*H*-1,2,4-triazole [5]. Kuhn and Kratz [11] proposed an improved synthesis of imidazol-2-ylidenes via reduction of imidazole-2(3*H*)-thiones with potassium in boiling THF. Important steps in this line were also syntheses of saturated heterocyclic carbenes, acyclic carbenes, and some multidentate systems [6].

We previously reported [12, 13] that C–H-insertions of heteroaromatic benzimidazol-2-ylidenes generated *in situ* with acetonitrile lead to the formation of the corresponding 2-cyanomethyl derivatives. A short time later, Arduengo et al. [14] described analogous reactions of nonaromatic 1,3-dimesityl-4,5-dihydroimidazol-2-ylidene with acetylene, dimethyl sulfone, and acetonitrile [14]. On the other hand, 1,3-dimesityl- and 1,3-diadamantyl-substituted imidazol-2-ylidenes failed to react with the same compounds. We presumed that the above dihydrodiazole derivatives may be intermediate products in the thermal synthesis of stable heteroaromatic carbenes. The first results obtained in this line were briefly reported in [13]. We also found that deprotonation of 1,2,4-triazolium salts with sodium hydride in acetonitrile can be used for direct

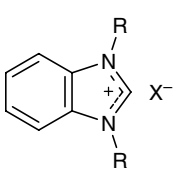
synthesis of 1,2,4-triazol-5-ylidenes [15]. Under more severe conditions (100°C), 1,2,4-triazol-5-ylidenes did react with acetonitrile to produce 5-cyanomethyl-4,5-dihydro-1*H*-1,2,4-triazoles.

With a view to estimate the possibility for preparation of stable carbenes of the benzimidazole and related imidazole series, as well of dihydroazole structures based thereon, we examined reactions of a number of benzimidazolium and imidazolium salts with sodium hydride in acetonitrile. In the present publication we report the following main results: (1) a new synthesis of a stable carbene, 1,3-bis(1-adamantyl)-benzimidazol-2-ylidene; (2) detailed synthesis of 1,3-disubstituted 2-cyanomethyl-2,3-dihydro-1*H*-benzimidazoles and 2-cyanomethyl-1,3,4,5-tetraphenyl-2,3-dihydro-1*H*-imidazole; (3) X-ray diffraction data for 1,3-bis(1-adamantyl)benzimidazol-2-ylidene, carbene precursors [the corresponding benzimidazolium salt, 1,3-disubstituted 2-cyanomethyl-2,3-dihydro-1*H*-benzimidazoles, 2-cyanomethyl-1,3,4,5-tetraphenyl-2,3-dihydro-1*H*-imidazole, 1-(1-adamantyl)-2-cyanomethyl-3,4-diphenyl-4,5-dihydro-1*H*-1,2,4-triazole], and 1,3-bis(1-adamantyl)- and 1,3-dibenzylimidazole-2-thiones; and (4) reactions of 1,3-bis(1-adamantyl)benzimidazol-2-ylidene with acetonitrile and sulfur.

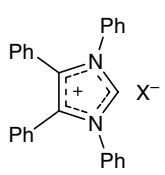
As carbene precursors we used the corresponding azolium salts. Benzimidazolium perchlorates **Ia**–**Ic** were synthesized in two steps. Initially, the corresponding benzimidazolium halides were prepared by alkylation of azoles with alkyl halides (methyl iodide, benzyl chloride, and 1-adamantyl bromide) in methanol (**Ia**) or in acetic acid in the presence of sodium acetate (**Ib**, **Ic**) or by reaction of 1-(1-adamantyl)-1*H*-benzimidazole with 1-adamantyl bromide in dichlorobenzene (**Ic**). The synthesis of adamantyl-substituted imidazoles, benzimidazoles, and benzimidazolium salts was described in [16]. The second step was anion exchange reaction performed by treatment of azolium halides with an aqueous solution of sodium perchlorate. Crystallization of benzimidazolium perchlorate **Ic** from dichloroethane gave crystals suitable for X-ray analysis. Salt **II** was obtained by oxidation of 1,3,4,5-tetraphenyl-2,3-dihydro-1*H*-imidazole-2-thione with nitric acid according to [17], followed by anion exchange reaction.

We have found that benzimidazolium salts **Ia**–**Ic** and imidazolium salt **II** having no substituent at the 2-position react with sodium hydride in acetonitrile at room temperature to give products of carbene insertion into the C–H bond of acetonitrile, 2-cyanomethyldihydroazoles **IIIa**–**IIIc** and **IV**. Compounds **IIIa**–**IIIc** and **IV** were isolated as crystalline substances and were characterized by the data of elemental analysis and IR and ^{1}H and ^{13}C NMR spectroscopy (see Experimental). In the ^{1}H NMR spectra of **IIIa**, **IIIb**, and **IV**, signals from protons in the CH–CH_2 fragment appeared as doublets at δ 2.67–3.23 ppm (CH_2) and triplets at δ 4.27–5.23 ppm (CH, ^3J = 2.8–6.0 Hz). Their ^{13}C NMR spectra contained signals from aromatic carbon atoms (δ_C 106.5–148.6 ppm) and carbon atoms of the cyano (δ_C 116.3–122.4 ppm), CHN (δ_C 86.3–86.7 ppm), and CH_2 groups (δ_C 27.8–34.9 ppm). Compounds **IIIa**, **IIIb**, and **IV** showed in the IR spectra (Nujol) absorption bands corresponding to aromatic C=C (1595–1600, 1480–1495 cm^{-1}) and C–H bonds (3045–3070 cm^{-1}) and C≡N group (2235–2240 cm^{-1}). The purity of **IIIa**, **IIIb**, and **IV** was checked by TLC and ^{1}H NMR.

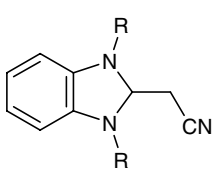
As shown above, carbene insertion into the C–H bond of acetonitrile occurs even in the reaction with sterically hindered 1,3-(1-adamantyl)benzimidazolium salt **Ic** where the C^2–H bond is shielded by bulky adamantane fragments. However, the product whose composition corresponded to 2-cyanomethyl derivative **IIIc** resembled ionic compounds in its chromatographic behavior. Like ionic species, it is poorly soluble in organic solvents (even in such a strongly polar solvent as DMSO). Compound **IIIc** underwent decomposition on heating in benzene or DMSO. The spectral parameters of **IIIc** somewhat differed from those of compounds **IIIa**, **IIIb**, and **IV**. Although the ^{1}H NMR spectrum of benzimidazole **IIIc** in DMSO-d_6 contained a triplet at δ 5.27 ppm (CH), as in the spectra of **IIIb** and **IV**, the CH_2CN signal appeared in a stronger field (δ 1.98 ppm) as a doublet (J = 5.8 Hz). Considerable shielding of the CH_2 protons may be caused by strong



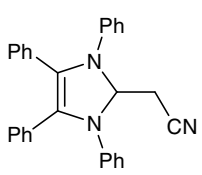
Ia–Ic



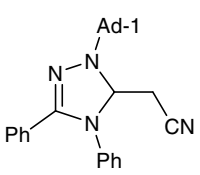
II



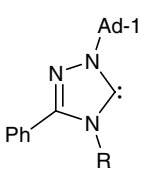
IIIa–IIIc



IV



V



VI

I, **III**, R = Me (**a**), Bzl (**b**), 1-Ad (**c**); **VI**, R = *p*-BrC_6H_4; X = ClO_4.

Table 1. Selected bond lengths (pm) and bond and torsion angles (deg) in the molecules of 1,3-dibenzyl-2,3-dihydro-1*H*-benzimidazol-2-ylacetonitrile (**IIIb**), 1,3-bis(1-adamantyl)-2,3-dihydro-1*H*-benzimidazol-2-ylacetonitrile (**IIIc**), and 1,3,4,5-tetraphenyl-2,3-dihydro-1*H*-imidazol-2-ylacetonitrile (**IV**)

Bond or angle	**IIIb**[a]	**IIIc**	**IV**[b]
C^2–N^1	145.9(2)	147.6(3)	146.6(3)
C^2–N^3	145.9(2)	146.2(3)	147.9(3)
C^5–N^1	139.4(2)	143.9(3)	145.3(3)
C^4–N^3	139.5(2)	139.6(3)	142.0(3)
C^4–C^5	140.4(2)	141.1(3)	136.4(3)
C^2–C^6	153.9(2)	154.8(3)	153.5(3)
N^1–C^{10}	146.3(2)[c]	150.7(3)	143.0(3)
$N^1C^2N^3$	103.7(1)	106.0(2)	105.0(2)
$C^2N^1C^5$	109.0(1)	102.4(2)	104.5(2)
$N^1C^5C^4$	108.6(1)	110.4(2)	108.9(2)
$C^2C^6C^7$	110.8(1)	111.5(2)	110.9(2)
$C^2N^1C^5C^4$	5.2(2)	17.0(2)	18.8(3)
$N^1C^2C^6C^7$	57.5(2)	65.0(2)	64.9(3)

[a] Other bonds: N^3–C^{16} 145.8(2), C^9–C^{10} 152.0(2), C^{16}–C^{20} 151.5(2) pm.

[b] Other angles: $C^2N^1C^{10}C^{11}$ 54.3(3), $C^4N^3C^{20}C^{21}$ 158.2(3), $N^3C^4C^{30}C^{31}$ –50.1(3), $N^1C^5C^{40}C^{41}$ 178.8(2)°.

[c] N^1–C^9 bond.

steric effect of the adamantyl substituents, especially of the nearest C–H bonds. The aromatic protons in **IIIc** give only one multiplet at δ 6.82 ppm, i.e., in a weaker field relative to the corresponding signals of **IIIa** and **IIIb** (Δδ = 0.4 ppm) and in a stronger field relative to those of salt **Ic** (Δδ = 0.8–1.2 ppm). An analogous pattern was observed in the spectra of some dihydroazoles having no substituent in the 2-position, as compared to the corresponding azolium salts [18, 19]. The C^2 signal in the ^{13}C NMR spectrum of **Ic** is displaced upfield relative to analogous signals of **IIIa**, **IIIb**, and **IV** ($\Delta\delta_C$ = 15.1–15.5 ppm), while the chemical shifts of the CN and CH_2 carbon nuclei are similar to those in **IIIa** and **IV**. These data indicate anisotropic shielding of the C^2 atom and CH_2 protons in molecule **IIIc**; i.e., dihydroazole **IIIc** is a sterically hindered compound. We thus presumed that compound **IIIc** exists in a polarized form with extended C^2–C^6 bond.

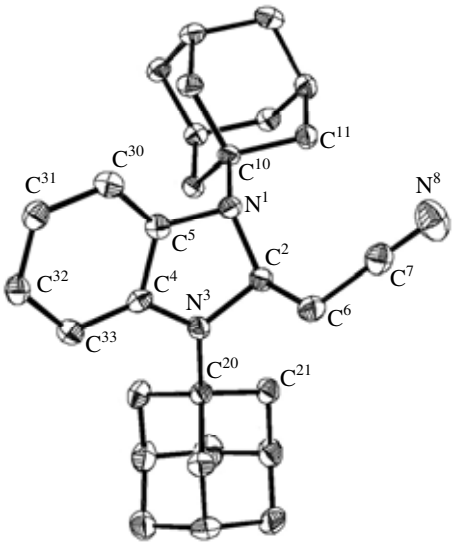


Fig. 1. Structure of the molecule of 1,3-bis(1-adamantyl)-2,3-dihydro-1*H*-benzimidazol-2-ylacetonitrile (**IIIc**) according to the X-ray diffraction data.

To verify the above assumption, the structure of compounds **IIIb**, **IIIc**, and **IV** was studied by the X-ray diffraction method (Table 1; Figs. 1, 2). Single crystals of **IIIc** were obtained by crystallization from benzene-d_6, and single crystals of **IIIb** and **IV**, by crystallization from acetonitrile. Compound **IV** crystallized as solvate $(C_{29}H_{23}N_3)_2 \cdot 4\,CH_3CN$. We have found no published X-ray diffraction data for 2-cyanomethyl derivatives of dihydroazoles.

The structures of molecules **IIIc** and **IV** are asymmetric with respect to the plane passing through the C^2 atom and mid C^4–C^5 bond. The C^2–C^6 bond declines toward one of the nitrogen atoms; therefore, the C^5–N^1/C^4–N^3 and C^2–N^1/C^2–N^3 bond lengths are slightly different in pairs. The dihydroimidazole fragment $N^3C^4C^5N^1$ is almost planar, but the C^2 atom deviates from that plane by an angle of 17.0–18.8°. The benzene ring attached to C^5 in structure **IV** is almost coplanar to the $N^3C^4C^5N^1$ fragment, while the other benzene rings with the $N^3C^4C^5N^1$ plane form dihedral angles of 22 to 54°. The C^2–C^6 bond in **IIIc** is slightly longer (d = 154.8 pm), and the $N^1C^2N^3$ bond angle is larger (106.0°), than the corresponding parameters of molecules **IIIb** and **IV** (153.9, 153.5 pm and 103.7, 105.0°, respectively).

Unlike structures **IIIc** and **IV**, the molecule of compound **IIIb** is symmetric with respect to the plane passing through the C^2 atom and mid C^4–C^5 bond (Fig. 3). The heteroring in **IIIb** is characterized by the least deviation from planarity (the $C^2N^1C^5C^4$ dihedral angle is 5.2°) among the examined cyanomethyl derivatives. All endocyclic bonds C^5–N^1, C^4–N^3, C^2–N^1, and C^2–N^3 are shorter than in molecules **IIIc** and **IV**. Specific attention should be given to shortening of the N^1–C^9 (146.3 pm) and N^3–C^{16} bonds relative to standard C–N bond (N^1–C^{10} 150.7 pm), which may be due to elec-

tron-withdrawing effect of the benzyl group. It should also be noted that the C^2–$N^{1(3)}$ bonds in molecules **IIIa**–**IIIc** are slightly shorter than standard single C–N bond.

We compared the X-ray diffraction data for dihydrobenzimidazoles **IIIb** and **IIIc** and dihydroimidazole **IV** with those for dihydrotriazole **V** (which was synthesized previously [15]); the structure of **V** was also compared with the structure of related carbene **VI** (Table 2; Figs. 3, 4). Crystals of compounds **V** and **VI** suitable for X-ray analysis were obtained by crystallization from acetonitrile and toluene, respectively. The distances C^5–N^1 and C^5–N^4 in molecule **V** were similar to those in **IIIb**, **IIIc**, and **IV**. The C^5–C^6 bond length (153.3 pm) and $N^1C^5N^4$ angle turned out to be the lowest among the examined cyanomethyl derivatives. All single bonds in carbene **VI** (C–N and N–N) are shorter by 2–5 pm, and the double C^3=N^2 bond is longer by 2 pm, than the corresponding bonds in molecule **V**, indicating higher aromaticity of the carbene structure. The N^4–C^{30} bond in **V** is shorter than the standard C–N bond; this means that the aromatic ring on N^4 is conjugated with the heteroring to the greatest extent.

Thus we obtained first information on the structure of insertion products formed by stable heteroaromatic benzimidazol-2-ylidenes and imidazol-2-ylidene. The insertion product of 1,2,4-triazol-5-ylidene was described previously [15]. C–H-Insertion reactions of the saturated 1,3-diphenyl-4,5-dihydroimidazol-2-ylidene dimer with cyclopentanone, nitromethane, and malononitrile were reported in [20, 21]. However, the products were not identified unambiguously, and it remained unclear whether the observed reactions involved monomeric or dimeric carbene species. Apart from publications [12–14], the problem concerning the reactivity of heteroaromatic carbenes toward acetonitrile was discussed by some other authors; but the corresponding insertion products were not isolated [6]. An unsuccessful attempt to react imidazol-2-ylidenes with acetonitrile was also reported in [10]. According to [5], attempts to isolate C–H-insertion products of triphenyl-substituted 1,2,4-triazol-5-ylidene were unsuccessful, for such reactions require elevated temperatures (>150°C) which promote decomposition of the carbene. Unsaturated heteroaromatic 1,3-bis(1-adamantyl)imidazol-2-ylidene also failed to react with acetonitrile, but its solvate with CH_3CN was formed instead [14].

As postulated in [22], carbenes are capable of being inserted into X–H bonds according to electrophilic and

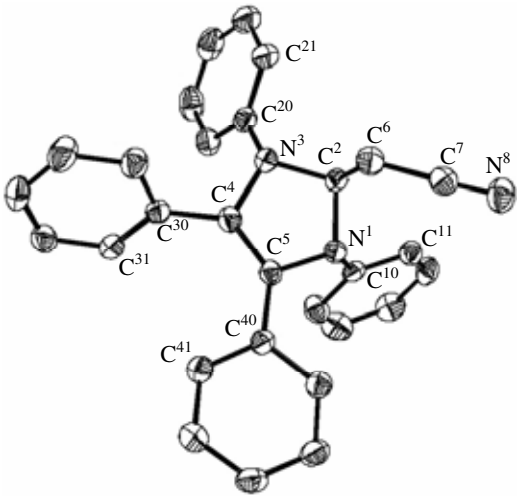


Fig. 2. Structure of the molecule of 1,3,4,5-tetraphenyl-2,3-dihydro-1*H*-imidazol-2-ylacetonitrile (**IV**) according to the X-ray diffraction data.

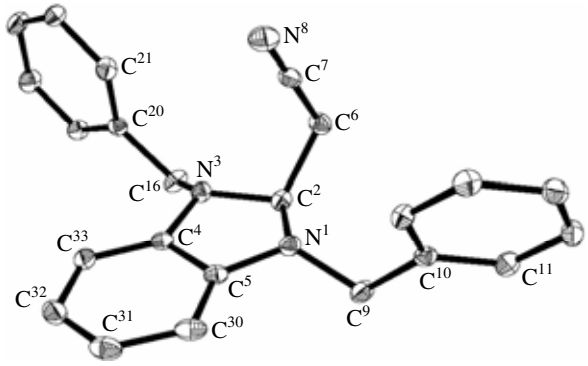


Fig. 3. Structure of the molecule of 1,3-dibenzyl-2,3-dihydro-1*H*-benzimidazol-2-ylacetonitrile (**IIIb**) according to the X-ray diffraction data.

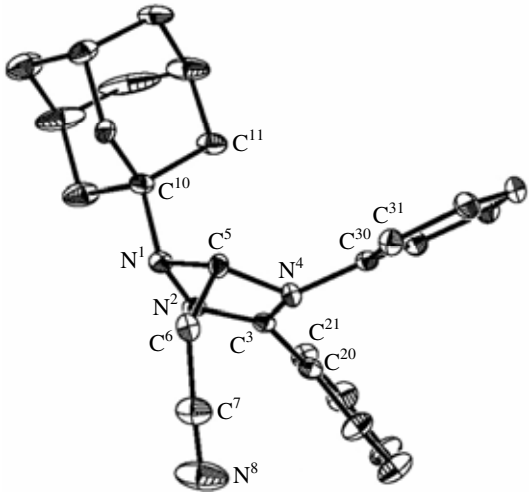


Fig. 4. Structure of the molecule of 1-(1-adamantyl)-3,4-diphenyl-4,5-dihydro-1*H*-1,2,4-triazol-5-ylacetonitrile (**V**) according to the X-ray diffraction data.

Table 2. Selected bond lengths (pm) and $N^1C^5N^4$ angles (deg) in the molecules of 1-(1-adamantyl)-3,4-diphenyl-4,5-dihydro-1*H*-1,2,4-triazol-5-ylacetonitrile (**V**) and 1-(1-adamantyl)-4-(4-bromophenyl)-3-phenyl-4,5-dihydro-1*H*-1,2,4-triazol-5-ylidene (**VI**)

Bond or angle	V	VI
C^5–N^1	148.5(4)	134.6(3)
C^5–N^4	147.1(4)	138.6(3)
C^3–N^4	140.5(4)	138.4(3)
C^3=N^2	128.2(4)	130.1(3)
N^1–N^2	144.4(4)	139.4(3)
C^3–C^{20}	147.6(5)	147.3(3)
N^4–C^{30}	141.9(4)	143.5(3)
C^5–C^6	153.3(5)	–
$N^1C^5N^4$	103.9(3)	100.3(2)

nucleophilic mechanisms (or, most probably, following an intermediate mechanism). Taking into account that benzimidazol-2-ylidenes are clearly nucleophilic, their reaction with acetonitrile should follow nucleophilic or mixed path, as shown in Scheme 1. An alternative version includes initial generation of $NCCH_2^-$ anion and its subsequent combination with azolium ion. To elucidate details of the reaction mechanism, we examined the reaction of 2-deuterio-1,3-dibenzylbenzimidazolium chloride (**Id**) with acetonitrile in the presence of sodium hydride. Salt **Id** was prepared by heating the corresponding ^{1}H-containing salt **Ib** in D_2O until the 2-H signal (δ 10.78 ppm) disappeared from the ^{1}H NMR spectrum. The transformation into 2-cyanomethyl derivative **IIIb** was accompanied by loss of deuterium, which indicated carbenoid mechanism of the process (Scheme 1).

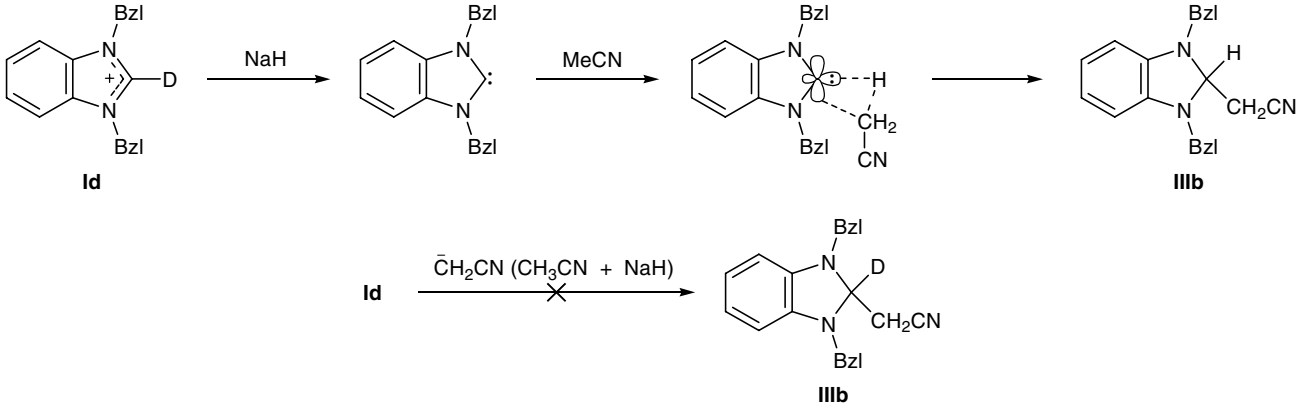
For comparison, it should be noted that acyclic phosphanylsilylcarbenes react with acetonitrile under analogous conditions to give azirines [23], while reactions of electrophilic *N*-fluoropyridylidene with nitriles and cyanates lead to the formation of pyrido[1,2-*a*]-[1,3,5]triazin-4-ones [24].

Compounds **IIIa**–**IIIc** and especially **IV** exhibit luminescence under UV irradiation. Taking into account the lack of conjugated substituents in structures **IIIa**–**IIIc**, this fact is surprising; it resembles luminescence of N-phenyl-substituted nonaromatic 4,5-dihydropyrazoles. Neither benzimidazole nor its quaternary salts **Ia**–**Ic** show even weak luminescence in the visible region. A probable reason is the presence of specific conjugation system (NCCN) in dihydroazole molecules **III** and **IV**.

2-Cyanomethyl derivatives **IIIa**–**IIIc** and **IV** are relatively stable on storage; they remained almost unchanged at room temperature under argon for several months. Compound **IIIc** was found to undergo decomposition on heating to 180°C under reduced pressure to give pure carbene **VIIa** (colorless powder) in high yield (method *a*). Analogous results were obtained by heating in aromatic solvents (benzene, toluene), but the process took a longer time. Although additional polarization and extension of the C^2–C^6 bond in molecule **IIIc** are weak (Δd = 13 pm), these factors are likely to favor dissociation of that bond on heating. Sterically unhindered dihydroazoles **IIIa**, **IIIb**, and **IV** undergo thermal decomposition in a complex manner; as a result, unidentified tarry products are formed.

Thus we were the first to isolate an individual stable carbene of the benzimidazole series (compound **VIIa**, mp 198–202°C). The product can be recrystallized from toluene and can be stored for several months at room temperature under argon without appreciable decomposition. Carbene **VIIa** can also be obtained by treatment of salt **Ic** in toluene with potas-

Scheme 1.



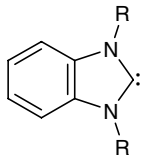
sium *tert*-butoxide at 80°C (the initial salt is poorly soluble in toluene). It is seen that the synthetic approaches to 1,2,4-triazol-5-ylidenes [15] are also effective in the synthesis of carbene **VIIa**.

All signals from aromatic protons and protons in the adamantyl substituents in the ^{1}H NMR spectrum of compound **V** in benzene-d_6 are displaced upfield relative to the corresponding signals of salt **Ic** ($\Delta\delta$ = 0.4–0.6 ppm), while no 2-H signal (typical of **Ic**) is present. The ^{13}C NMR spectrum contains a signal at δ_C 223.0 ppm, which belongs to the carbene carbon atom, signals from carbon atoms in the adamantyl groups (δ_C 29.5–57.5), and aromatic carbon signals (δ_C 113.7–134.8 ppm). The IR spectrum of dihydroazole **V** in Nujol resembles those reported for 1,2,4-triazol-5-ylidenes [15]: the most typical are absorption bands due to stretching vibrations of C–H and C=C bonds at 3035 and 1600, 1500 cm^{-1}, respectively.

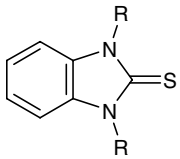
The reaction reverse to the decomposition **IIIc** → **VIIa**, i.e., insertion **VIIa** → **IIIc**, is fairly fast: the conversion of carbene **VIIa** in acetonitrile is complete in several minutes, and in toluene, in 15–30 min at room temperature.

Thus the insertion into the C–H bond of acetonitrile effectively occurs with strongly basic heteroaromatic carbenes (aryl-substituted imidazol-2-ylidenes and benzimidazol-2-ylidenes having aliphatic substituents); analogous reactions with 1,2,4-triazol-5-ylidenes are much slower [15]. We also synthesized a new heteroaromatic carbene, benzimidazol-2-ylidene **VIIa**, which is stable on prolonged storage.

Almost simultaneously with us [13], Hahn et al. [25] synthesized another carbene of the benzimidazole series, 1,3-dineopentylbenzimidazol-2-ylidene (**VIIb**), by reduction of the corresponding thione with sodium–potassium alloy at room temperature (reaction time 20 days). However, compound **VIIb** is a mixture of stereoisomers, and it has a low melting point, 26°C. The synthesis of **VIIb** is much more difficult than the synthesis of high-melting carbene **VIIa**; in addition, the latter is a single isomer and is more convenient to handle with.



VIIa, **VIIb**



VIIIa, **VIIIb**

VII, R = 1-Ad (**a**), *t*-BuCH$_2$ (**b**); **VIII**, R = 1-Ad (**a**), Bzl (**b**).

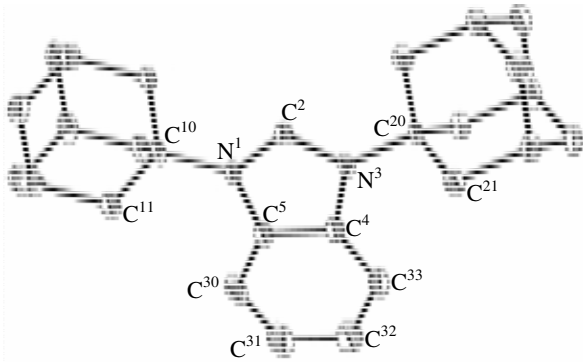


Fig. 5. Structure of the molecule of 1,3-bis(1-adamantyl)-benzimidazolium perchlorate (**Ic**) according to the X-ray diffraction data.

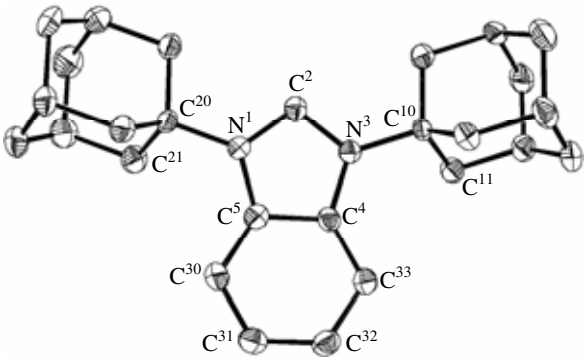


Fig. 6. Structure of the molecule of 1,3-bis(1-adamantyl)-2,3-dihydro-1*H*-benzimidazol-2-ylidene (**VIIa**) according to the X-ray diffraction data.

Crystals of carbene **VIIa** for X-ray analysis were grown from a solution in anhydrous toluene. For comparison, we also performed X-ray analysis of perchlorate **Ic**; single crystals of the latter were obtained by crystallization from dichloroethane. The structural parameters of compounds **VIIa** and **Ic** are given in Table 3, and their molecular structures are shown in Figs. 5 and 6. It is seen that the bonds at the carbene center in **VIIa** (C^2–$N^{1(3)}$ ~137 pm) are appreciably longer than in azolium salt **Ic** (Δd = 3.8 pm) (Fig. 4) and appreciably shorter than the ordinary $N^{1(3)}$–$C^{10(20)}$ bond (149–150 pm). These data suggest electron density delocalization in the carbene molecule. The corresponding bonds in salt **Ic** are also delocalized, but their lengths are closer to those of typical double bonds (d = 132.2, 133.6 pm). The benzimidazole fragment in molecule **VIIa** is almost planar due to conjugation. For comparison, Table 3 also contains crystallographic data for Hahn's carbene **VIIb** [25].

The structural parameters of molecules **VIIa** and **VIIb** are fairly similar, but the C^2–N^1 and C^5–N^1 bonds in **VIIa** are slightly longer (Δd = 0.8–1.4 pm), while

Table 3. Selected bonds lengths (pm) and bond angles (deg) in the molecules of compounds **Ic** and **VII**,[a] 1,3-bis(1-adamantyl)-2,3-dihydro-1*H*-imidazol-2-ylidene (**IX**) [3],[b] carbene **VIIb** [25], and thiones **VIIIa** and **VIIIb**

Bond or angle	**Ic**	**VIIa**	**VIIb**		**VIIIa**	**VIIIb**	**IX**
			A	*B*			
C^2–N^1	133.6(4)	137.4(4)	136.1(2)	136.0(2)	138.9(2)	136.7(2)	136.5(4)
C^5–N^1	139.9(4)	140.2(4)	139.4(2)	139.4(2)	140.4(2)	139.0(2)	138.1(4)
C^5–C^4	141.5(4)	139.8(4)	139.5(2)	138.6(2)	140.3(3)	139.8(3)	133.5(5)
N^1–C^{10}	148.9(4)	149.3(4)	145.8(2)	145.8(2)	152.1(2)	146.5(2)	144.1(4)
$N^1C^2N^3$	112.2(3)	103.8(2)	103.5(1.3)	104.3(1.4)	108.14(15)	106.37(19)	101.4(2)
$C^2N^1C^5$	107.6(2)	112.2(2)	112.8(1.2)	112.0(1.4)	108.27(15)	110.30(14)	112.8(3)
$N^1C^5C^4$	106.9(2)	105.8(2)	–	–	107.80(15)	106.51(9)	106.5(3)

[a] Other bond lengths, pm: **Ic**: C^2–N^3 132.2(4), C^4–N^3 139.6(4), N^3–C^{20} 150.0(4); **VII**: C^2–N^3 137.2(4), C^4–N^3 139.9(4), N^3–C^{20} 149.4(3); **VIII**: C^2–S 168.05(19) (**a**), 168.0(2) (**b**).

[b] Data for 1,3-bis(1-adamantyl)-2,3-dihydro-1*H*-imidazol-2-ylidene.

the N^1–C^{10} bond is appreciably longer (Δd = 3.5 pm). The difference in the C^5–N^1 and N^1–C^{10} bond lengths increases in going to 1,3-bis(1-adamantyl)imidazol-2-ylidene (**IX**). The observed variations originate from steric effects of the bulky adamantyl groups and fused benzene ring, which make carbene **VIIa** less aromatic than **VIIb** and **IX** [3]. We determined the bond angles in the benzimidazol-2-ylidene fragment with a higher accuracy as compared to [25] (Table 3).

All bonds in carbene **VIIa** are shorter than the corresponding bonds in **IIIc** due to aromatic character of the carbene ring. The C^4=C^5 bond in **VIIa** is also appreciably shorter, indicating lesser bond leveling than in **VI**; the C^3=N^2 bond in the latter is longer than in dihydroazole **V**. These findings may be interpreted in terms of higher aromaticity of 1,2,4-triazol-5-ylidenes compared to benzimidazol-2-ylidenes. On the other hand, our experimental data and the results of theoretical calculations [26] suggest similar aromaticities of benzimidazol-2-ylidenes and 1,2,4-triazol-5-ylidenes in keeping with the delocalization criterion; the latter are only slightly more aromatic.

The endocyclic $N^1C^2N^3$ angle in molecule **VIIa** (103.8°) is considerably smaller than in salt **Ic** ($\Delta\omega$ = 8.4°) due to repulsion between sp^2-electrons at the carbene carbon atom and electrons at the endocyclic C–N bonds. The $N^1C^2N^3$ angle is intermediate between imidazol-2-ylidenes (101–102°) [3, 4] and dihydroimidazol-2-ylidene **VI** (104.7–106.4°) [18], but it appreciably exceeds the corresponding bond angle in 1,2,4-triazol-5-ylidenes (100.3°) [5, 15]. Presumably, the bond angle at the carbene carbon atom reflects stabilization of nucleophilic cyclic carbenes via aromatic delocalization; this parameter indicates higher aromaticity of 1,2,4-triazol-5-ylidenes.

As noted above, nucleophilic carbene **VIIa** is much more reactive than triazolylidenes toward acetonitrile. We examined reactions of **VIIa** with sulfur and selenium in benzene. The reaction with sulfur was very fast (1–2 min at room temperature), and it resulted in the formation of thione **VIIIa** and intensely red–brown compound **X**. The composition of the latter was determined as $(C_{27}H_{34}N_2)_2S_7\cdot 4C_6H_6$, i.e., it is a solvate with benzene. Presumably, it has a structure like Crb^+–$S^-(S^+{=}S^-)_3$=Crb, where Crb is the carbene **VIIa** fragment as azolium ion (Crb^+) or dihydroazole (=Crb). We succeeded in isolating compound **X** due to its poor solubility in benzene; the product separated from the reaction mixture during the process. Compound **X** is very sensitive to atmospheric oxygen and moisture: on dissolution in chloroform, it is converted into colorless thione **VIIIa** (16%) and pale yellow salt **Ic** with $HS_3O_4^-$ as counterion (60%). Anion exchange reaction of the latter with sodium perchlorate gave perchlorate **Ic** described above. We failed to record IR or NMR spectra of **X** and determine its crystalline structure because of its fast transformation in polar solvents. Judging by the elemental composition, color, and chemical behavior, product **X** can be regarded as a hypervalent sulfur compound. The yield of thione **VIIIa** strongly depends on the reactant ratio: it changes from 49% in the reaction with excess carbene to 90% with excess sulfur. Obviously, the reason is the formation of compound **X**. Our failure to isolate a product like **X** in the reactions of 1,2,4-triazol-5-ylidenes with sulfur [15] may be explained by its fast

decomposition in solution to the corresponding 1,2,4-triazole-5-thione.

Crystals of thione **VIIIa** for X-ray analysis were obtained from a solution in DMF. With a view to compare its structure with that of a related sterically unhindered thione, we synthesized 1,3-dibenzylbenzimidazole-2-thione by heating perchlorate **Ib** with sulfur in acetonitrile in the presence of triethylamine. Single crystals of thione **VIIIb** were grown from a solution in propan-2-ol. The NMR spectra of thiones **VIIIa** and **VIIIb** were essentially similar (see Experimental). The most characteristic signals from C^2 in the ^{13}C NMR spectra of **VIIIa** and **VIIIb** were located at δ_C ~170.8 ppm.

According to the X-ray diffraction data, adamantyl-substituted thione **VIIIa** is characterized by longer endocyclic C–N bonds as compared to **VIIIb**, presumably due to electron-donor effect of the 1-adamantyl groups. The same factor is likely to be responsible for the shorter exocyclic N–C_{Bzl} bonds in **VIIIb** relative to the corresponding bonds in molecule **VIIIa**. The C–S distances in the molecules of both compounds are equal. This fact indicates the absence of appreciable steric shielding of the sulfur atom. The $N^1C^2N^3$ angle in molecule **VIIIa** is larger than in **VIIIb**; a probable reason is steric repulsion between hydrogen atoms in the fused benzene ring and adamantyl substituent in molecule **VIIIa**.

Unlike the reaction with sulfur, selenium failed to react with carbene **VIIa** under analogous conditions. Presumably, the reaction is hampered by steric hindrances to the formation of intermediate hypervalent selenium compound from cyclic molecular selenium (but not atomic selenium whose radius is only slightly larger than that of sulfur: S 1.04, Se 1.17 Å). As far as we know, this is the first example of strong steric hindrances to carbene reactions with chalcogens.

EXPERIMENTAL

All experiments with benzimidazol-2-ylidene **VIIa** and with carbenes generated *in situ* were carried out under argon. The solvents were dried by standard procedures. The NMR spectra were recorded on a Varian Gemini-200 spectrometer at 200 (^1H) and 50.3 MHz (^{13}C) using tetramethylsilane as internal reference. The IR spectra were measured in Nujol on a Specord 75IR spectrometer. Thin-layer chromatography was performed on silica gel using chloroform or chloroform–methanol (10 : 1) as eluent; development with iodine vapor.

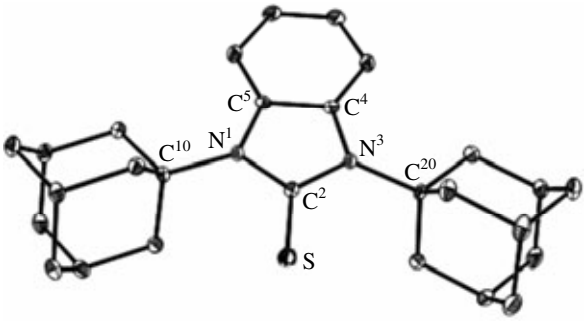


Fig. 7. Structure of the molecule of 1,3-bis(1-adamantyl)-2,3-dihydro-1*H*-benzimidazole-2-thione (**VIIIa**) according to the X-ray diffraction data.

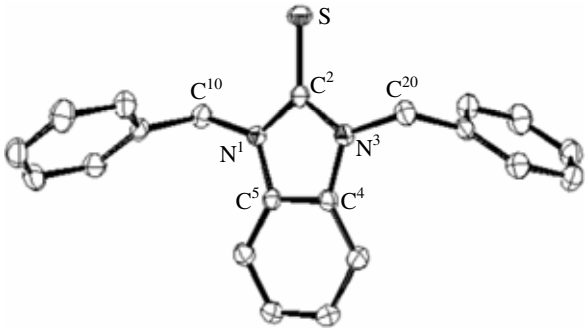


Fig. 8. Structure of the molecule of 1,3-dibenzyl-2,3-dihydro-1*H*-benzimidazole-2-thione (**VIIIb**) according to the X-ray diffraction data.

X-Ray analysis was performed on a Nonius-Kappa CCD diffractometer [λ 0.71069–0.71073 Å; temperature 153(2) K] with no correction for absorption. The results of measurements were treated by the full-matrix least-squares procedure with respect to F^2. The principal crystallographic parameters of the examined compounds are given in Table 4. The calculations were performed according to manuals [27] (data acquisition and cell refinement), [28] (data reduction), [29] (structure resolution), and [30] (structure refinement and molecular graphics). The complete sets of the crystallographic data are available from the authors.

2,3-Dihydro-1*H*-(benz)imidazol-2-ylacetonitriles IIIa–IIIc and IV (*general procedure*). Sodium hydride (separated from mineral oil), 0.026 g (1.1 mmol), was added in one portion under argon to a solution of 1 mmol of azolium salt **Ia–Ic** or **II** in anhydrous acetonitrile (5–50 ml). The mixture was stirred for 0.5–1 h (**IIIa**, **IIIb**, **IV**), the progress of the reaction being monitored by the volume of evolved hydrogen. The mixture was then passed under argon through a thin layer of degassed neutral silica gel, and the solvent was removed under reduced pressure. The oily residue was ground with hexane, and the precipitate was filtered

Table 4. Principal crystallographic parameters and conditions of X-ray diffraction experiments for compounds **Ic**, **IIIb**, **IIIc**, **IV**, **V**, **VII**, **VIIIa**, and **VIIIb**

Parameter	Ic	IIIb	IIIc	IV	V	VIIa	VIIIa	VIIIb
Crystal system	Orthorhombic	Monoclinic	Triclinic	Triclinic	Orthorhombic	Monoclinic	Monoclinic	Monoclinic
Space group	*Pbca*	$P2_1/n$	*P*-1	*P*-1	$P2_12_12_1$	$P2_1/c$	*C*2/*c*	*C*2/*c*
a, Å	18.047(4)	8.120	9.968(2)	13.428(3)	10.892(5)	12.233(5)	21.1300(3)	18.6940(2)
b, Å	12.858(3)	18.031	10.847(2)	14.379(3)	11.031(5)	11.768(5)	10.4150(2)	9.7410(2)
c, Å	26.796(5)	12.404	11.484(2)	15.519(3)	36.066(5)	14.737(5)	21.8010(3)	9.9250(2)
α, deg	90.000(5)	90	97.02(3)	93.55(3)	90.000(5)	90.000(5)	90.000(5)	90.000(10)
β, deg	90.000(5)	94.29	107.80(3)	114.05(3)	90.000(5)	93.716(5)	90.000(5)	111.0930(10)
γ, deg	90.000(5)	90	102.99(3)	91.79(3)	90.000(5)	90.000(5)	90.000(5)	0.000(10)
Crystal habit, mm	0.2×0.2×0.2	0.4×0.3×0.3	0.2×0.2×0.2	0.2×0.2×0.2	0.3×0.3×0.3	0.3×0.2×0.2	0.4×0.3×0.2	0.3×0.3×0.2
Total number of reflections	23980	7681	8768	18905	12314	9506	4847	1917
Number of independent reflections	8631	4135	5173	12304	8509	5712	4847	1917
Completeness, %	91.1	99.2	98.9	98.9	77.3	88.7	99.3	99.0
θ, deg	30.06	30.47	30.47	27.44	30.06	30.47	30.06	30.06
Goodness of fit (by F^2)	1.005	1.169	0.754	1.014	1.267	0.977	1.061	1.159
R_1 [$I > 2\sigma(I)$]	0.0766	0.0609	0.0542	0.0776	0.0978	0.0837	0.0495	0.0476
wR_2 [$I > 2\sigma(I)$]	0.2327	0.1181	0.1428	0.1582	0.1314	0.1850	0.1043	0.0861
R_1 (all reflections)	0.1379	0.0749	0.0985	0.1588	0.1266	0.1775	0.0803	0.0590
wR_2 (all reflections)	0.2603	0.1226	0.1820	0.1952	0.1405	0.2266	0.1216	0.0932

off, dried, and recrystallized. In the synthesis of compound **IIIc**, the reaction time was 4 h (25°C); the mixture was held for 0.5 h at 0°C, and the precipitate was filtered off and dried.

1,3-Dimethyl-2,3-dihydro-1*H*-benzimidazol-2-ylacetonitrile (IIIa). Yield 89%, R_f 0.79, mp 104–105°C (from MeCN). IR spectrum, ν, cm^{-1}: 3070 w (C–H), 2235 m (C≡N), 1595 m, 1495 m (C=C_{arom}), 1300 m, 1270 m, 1215 m, 1165 m, 1110 m, 1055 m, 1010 m, 730 s. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.63 s (3H, CH_3N), 2.83 d (2H, CH_2, ^3J = 3.0 Hz), 4.27 t (1H, 2-H, ^3J = 3.0 Hz), 6.47 m (4H, H_{arom}). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 23.2 (C^6), 34.9 (C^{10}, C^{20}), 86.7 (C^2), 116.3 (C^7), 106.5 (C^{31}, C ^{32}), 119.8 (C^{30}, C ^{33}); 141.6 (C^4, C^5). Found, %: C 70.5; H 6.9; N 22.7. $C_{11}H_{13}N_3$. Calculated, %: C 70.6; H 7.0; N 22.4.

1,3-Dibenzyl-2,3-dihydro-1*H*-benzimidazol-2-ylacetonitrile (IIIb). Yield 72%, R_f 0.87, mp 134–136°C (from MeCN). IR spectrum, ν, cm^{-1}: 3045 w (C–H), 2240 w (C≡N), 1600 m, 1495 m (C=C_{arom}), 1300 m, 1280 m, 1220 m, 1140 m, 1120 m, 1070 m, 1010 m, 730 s. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.67 d (2H, 2-CH_2, ^3J = 2.8 Hz), 4.27 s (2H, CH_2N), 5.00 t (1H, 2-H, ^3J = 2.8 Hz), 6.40 m (4H, H_{arom}), 7.27 m (10H, H_{arom}). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 24.8 (C^6), 53.3 (C^{10}, C^{20}), 83.0 (C^2), 116.3 (C^7), 106.9 (C^{31},

C ^{32}), 119.8 (C^{30}, C ^{33}), 137.2 (C^{11}, C^{21}), 141.0 (C^4, C^5). Found, %: C 81.2; H 6.3; N 12.4. $C_{23}H_{21}N_3$. Calculated, %: C 81.4; H 6.2; N 12.4.

1,3-Bis(1-adamantyl)-2,3-dihydro-1*H*-benzimidazol-2-ylacetonitrile (IIIc). *a*. Yield 79%, mp 187–189°C (from toluene–acetonitrile, 3:1). IR spectrum, ν, cm^{-1}: 3060 w (CH), 2235 m (C≡N), 1590 m (C=C$_{arom}$), 1300 m, 1280 m, 1240 m, 1190 m, 1170 m, 1080 m, 1035 m, 1025 m, 980 m, 730 s. ^{1}H NMR spectrum (C_6D_6), δ, ppm: 1.42 m (12H), 1.82 m (12H), 1.93 m (6H) (1-Ad); 1.98 d (2H, 2-CH$_2$, ^3J = 5.8 Hz), 5.27 t (1H, 2-H, ^3J = 5.8 Hz), 6.83 m (4H, H$_{arom}$). ^{13}C NMR spectrum (C_6D_6), δ$_C$, ppm: 26.8 (C^6), 30.1 (C^{12}, C^{14}, C^{16}, C^{22}, C^{24}, C^{26}), 36.6 (C^{13}, C^{15}, C^{19}, C^{23}, C^{25}, C^{29}), 41.3 (C^{11}, C^{17}, C^{18}, C^{21}, C^{27}, C^{28}) (1-Ad); 55.7 (C^{10}, C^{20}, 1-Ad), 71.2 (C^2), 118.0 (C^7), 116.2 (C^{31}, C^{32}), 120.3 (C^{30}, C^{33}), 139.0 (C^4, C^5). Found, %: C 81.9; H 8.7; N 9.8. $C_{29}H_{37}N_3$. Calculated, %: C 81.5; H 8.7; N 9.8.

b. Anhydrous acetonitrile, 2 ml, was added dropwise to a solution of 0.08 g (0.21 mmol) of carbene **VIIa** in 1 ml of anhydrous benzene. The mixture was stirred for 0.5 h, and the precipitate was filtered off, dried, and recrystallized as described above. Yield 0.08 g (90%). Analogous results were obtained in pure acetonitrile where the product is soluble very poorly. In this case, the reaction was complete in several minutes at room temperature, and the mixture was additionally stirred for 0.5 h.

1,3,4,5-Tetraphenyl-2,3-dihydro-1*H*-imidazol-2-ylacetonitrile (IV). Yield 55%, R_f 0.97, mp 143–144°C (from MeCN). IR spectrum, ν, cm^{-1}: 3050 w (C–H), 2235 w (C≡N), 1590 m, 1480 m (C=C$_{arom}$), 1300 m, 1255 m, 1115 m, 1040 m, 1020 m, 760 s. ^{1}H NMR spectrum (CD_3CN), δ, ppm: 3.23 d (2H, 2-CH$_2$, ^3J = 6.0 Hz), 5.23 t (1H, 2-H, ^3J = 6.0 Hz), 7.12 m and 7.60 m (10H each, H$_{arom}$). ^{13}C NMR spectrum (CD_3CN), δ$_C$, ppm: 27.8 (C^6); 86.3 (C^2); 122.4 (C^7); 124.4 (C^4, C^5); 129.1, 130.0, 130.4 (C$_{arom}$); 137.5 (C^{20}, C^{30}); 148.6 (C^{10}, C^{40}). Found, %: C 84.1; H 5.8; N 10.2. $C_{29}H_{23}N_3$. Calculated, %: C 84.2; H 5.6; N 10.2.

1,3-Bis(1-adamantyl)-2,3-dihydro-1*H*-benzimidazol-2-ylidene (VIIa). *a*. Compound **IIIc** was heated under reduced pressure, gradually raising the temperature from 100 to 180°C, and was then kept for 1–1.5 h at 180°C. The product was an almost colorless crystalline substance. Yield 91%, mp 198–202°C (from toluene). IR spectrum, ν, cm^{-1}: 3035 w (C–H$_{arom}$); 1600 w, 1500 w (C=C$_{arom}$). ^{1}H NMR spectrum (C_6D_6), δ, ppm: 1.60 m (12H), 2.04 m (6H), and 2.55 m (12H) (1-Ad); 7.07 d.d (2H), 7.66 d.d (2H, ^3J = 6.1, ^4J = 3.2 Hz) (H$_{arom}$). ^{13}C NMR spectrum (C_6D_6), δ$_C$, ppm: 29.5 (C^{12}, C^{14}, C^{16}, C^{22}, C^{24}, C^{26}), 36.0 (C^{13}, C^{15}, C^{19}, C^{23}, C^{25}, C^{29}), 42.5 (C^{11}, C^{17}, C^{18}, C^{21}, C^{27}, C^{28}) (1-Ad); 57.5 (C^{10}, C^{20}) 113.7 (C^{31}, C^{32}), 119.2 (C^{30}, C^{33}), 134.6 (C^4, C^5, C$_{arom}$), 223.0 (C^2). Found, %: C 84.0; H 8.9; N 7.1. $C_{27}H_{34}N_2$. Calculated, %: C 83.9; H 8.9; N 7.3.

b. Potassium *tert*-butoxide, 0.56 g (5 mmol), was added in one portion under argon to a suspension of 2.43 g (5 mmol) of benzimidazolium perchlorate **Ic** in 15 ml of anhydrous toluene. The mixture was stirred for 0.5 h, heated to 80°C, and cooled to room temperature, the precipitate of $KClO_4$ was filtered off, and the filtrate was evaporated under reduced pressure. Yield 1.71 g (82%), crystalline substance, mp 198–202°C (from toluene). The product was identical to a sample prepared as described above in *a*.

1,3-Bis(1-adamantyl)-2,3-dihydro-1*H*-benzimidazole-2-thione (VIIIa). A solution of 0.42 g (1.1 mmol) of carbene **VII** in 1 ml of anhydrous benzene was added dropwise under stirring to a solution of 0.049 g (1.56 mmol) of sulfur in 5 ml of anhydrous benzene. The precipitate, 0.02 g (5%) of by-product **X**, was filtered off, and the filtrate was evaporated under reduced pressure. Yield 0.41 g (90%), mp 275–276°C (from DMF). IR spectrum, ν, cm^{-1}: 3050 w (C–H$_{arom}$), 1700 m (N–C=S), 1600 m, 1555 m, 1500 m (C=C$_{arom}$). ^{1}H NMR spectrum, δ, ppm: in $CDCl_3$: 1.72 m (12H), 2.25 m (6H), and 2.42 m (12H) (1-Ad); 7.38 m and 7.82 m (2H each, H$_{arom}$); in pyridine-d_5: 1.55 m (6H), 1.74 m (6H), 2.08 m (6H), and 3.13 m (12H) (1-Ad); 7.05 m and 7.87 m (2H each, H$_{arom}$). ^{13}C NMR spectrum (pyridine-d_5), δ$_C$, ppm: 31.1 (C^{12}, C^{14}, C^{16}, C^{22}, C^{24}, C^{26}), 36.4 (C^{13}, C^{15}, C^{19}, C^{23}, C^{25}, C^{29}), 40.9 (C^{11}, C^{17}, C^{18}, C^{21}, C^{27}, C^{28}), 67.2 (C^{10}, C^{20}), 114.3 (C^{31}, C^{32}), 121.5 (C^{30}, C^{33}), 134.0 (C^4, C^5), 170.8 (C^2). Found, %: C 77.5; H 8.5; N 6.9; S 7.9. $C_{27}H_{34}N_2S$. Calculated, %: C 77.4; H 8.2; N 6.7; S 7.7.

Compound **X**. mp 150°C (decomp.). Found, %: C 71.8; H 7.0; N 4.3; S 17.3. $C_{54}H_{68}N_4S_7 \cdot 4C_6H_6$. Calculated, %: C 71.5; H 7.1; N 4.3; S 17.1.

1,3-Dibenzyl-2,3-dihydro-1*H*-benzimidazole-2-thione (VIIIb) was synthesized by heating equimolar amounts of perchlorate **Ib** and triethylamine and a small excess of sulfur (20%) in MeCN. mp 184°C (from *i*-PrOH). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 5.65 s (4H, CH_2N), 7.09 m (4H, H$_{arom}$), 7.33 m (10H, H$_{arom}$). ^{13}C NMR spectrum ($CDCl_3$), δ$_C$, ppm: 48.36 (CH_2N), 109.42 (C^6, C^7), 122.81 (C^5, C^8), 127.26 (C^p),

127.56 (C^o), 128.53 (C^m), 131.78 (C^{4a}, C^{7a}), 135.40 (C^i), 170.81 (C^2).

Oxidative decomposition of compound X. Compound **X**, 0.1 g (0.076 mmol), was dissolved in 1 ml of chloroform, and the solution was stirred for 20 min on exposure to air. The mixture was diluted with 2 ml of hexane, and the pale precipitate was filtered off and dried. Yield of salt **Ic** (X = HS_3O_4) 0.05 g (60%). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 1.84 m (12H), 2.37 m (6H), 2.54 m (12H) (1-Ad); 7.56 d.d (2H, H_{arom}), 8.01 d.d (2H, H_{arom}, ^3J = 6.5, ^4J = 3.2 Hz), 9.10 s (1H, 2-H). Found, %: C 59.3; H 6.5; N 5.3; S 17.6. $C_{27}H_{36}N_2S_3O_4$. Calculated, %: C 59.1; H 6.6; N 5.1; S 17.5.

Evaporation of the filtrate gave 0.01 g (16%) of thione **VIIIa** which was identical to a sample described above in the IR spectrum and melting point. By treatment of salt **Ic** (X = HS_3O_4) with excess aqueous sodium perchlorate we obtained initial salt **Ic** (X = ClO_4).

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