# Reactions of benzimidazole-2-carbaldehyde with enamines

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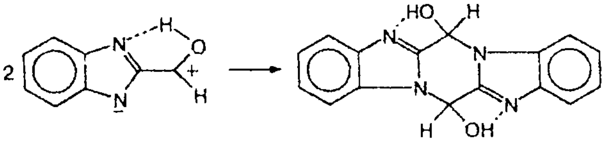
Benzimidazole-2-carbaldehyde reacts with 1-morpholinocyclohexene, 1-morpholinocyclopentene, and aminocrotonic ester upon heating to form 4a,11-dimorpholino-1,2,3,4,11,11a-hexahydro-4a*H*-indolo[1,2-*a*]benzimidazole, 2-(2-morpholino-4,5-dihydrofulvenyl)benzimidazole, and 4-(benzimidazol-2-yl)-3,5-diethoxycarbonyl-2,6-dimethyl-1,4-dihydropyridine, respectively.

**Key words:** benzimidazole-2-carbaldehyde, enamines, 1,3-dipolar cycloaddition, 4a,11-dimorpholino-1,2,3,4,11,11a-hexahydro-4a*H*-indolo[1,2-*a*]benzimidazole, 2-(2-morpholino-4,5-dihydrofulvenyl)benzimidazole, 4-(benzimidazol-2-yl)-3,5-diethoxycarbonyl-2,6-dimethyl-1,4-dihydropyridine.

Reactions of cycloaddition of enamines to various bipolar compounds is a promising field of the chemistry of heterocycles.[1] Condensation of enamines with substituted salicylaldehydes is a general procedure for the synthesis of heterocyclic systems containing pyran fragments.[2] One would expect that the replacement of substituted salicylaldehydes in these reactions with heterocyclic aldehydes that contain the imide hydrogen atom in the *ortho* position would afford new condensed nitrogen-containing heterocycles. For example, the reaction of benzimidazole-2-carbaldehyde with cyclohexanone enamines would be expected to give previously unknown derivatives of perhydroindolo[1,2-*a*]benzimidazole. However, it is known that the structure of benzimidazole-2-carbaldehyde does not correspond to the simplest formula. It is a high-melting and poorly soluble compound with a masked aldehyde function. The IR spectrum of this compound does not contain an absorption band of the aldehyde group. Based on the chemical and physical properties, we assigned the formula of cyclic hemiaminal **1** to the compound in question.[3] The formation of structure **1** can be represented as a result of complete transfer of the imide proton of benzimidazole-2-carbaldehyde to the oxygen atom of the aldehyde group and dimerization of this hypothetical 1,3-dipole **2** (Scheme 1).

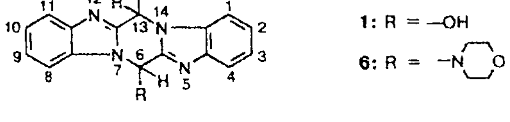
**Scheme 1**



**2** **1**

Previously, it has also been demonstrated[3] that the hydroxyl groups in compound **1** were readily replaced by amine fragments upon heating with secondary aliphatic amines. This indicates that the electrophilic character of the aldehyde carbon atoms in the dimer is retained, which is also confirmed by the results of our quantum-chemical calculations (Table 1). These atoms are electrophilic also in dimers containing amine groups instead

**Table 1.** Quantum-chemical PM3 calculations of the charge distributions ($q$) in compounds **1** and **6**



| Atom | $q$/e | | Atom | $q$/e | |
|---|---|---|---|---|---|
| | **1** | **6** | | **1** | **6** |
| 1,8 | −0.085 | −0.109 | 5,12 | −0.074 | −0.052 |
| 2,9 | −0.081 | −0.079 | 5a,12a | −0.221 | −0.175 |
| 3,10 | −0.122 | −0.121 | 6,13 | 0.198 | 0.065 |
| 4,11 | −0.031 | −0.029 | 7,14 | 0.213 | 0.140 |
| 4a,11a | −0.092 | −0.089 | 7a,14a | −0.137 | −0.146 |

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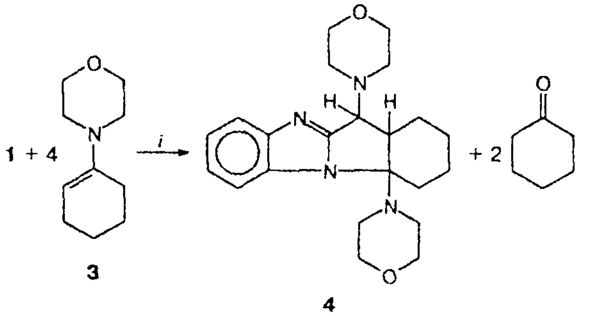
of hydroxyl fragments (in particular, *N*-morpholine groups), though charges are small.

We found that compound **1** smoothly reacted with 1-morpholinocyclohexene (**3**) upon heating to 140—160 °C to form 4a,11-dimorpholino-1,2,3,4,11,11a-hexahydro-4a*H*-indolo[1,2-*a*]benzimidazole (**4**), which is simultaneously a diazapentalene derivative (Scheme 2). To put it differently, the reaction proceeded in a manner which could be expected in the case of aldehyde containing the imide hydrogen.

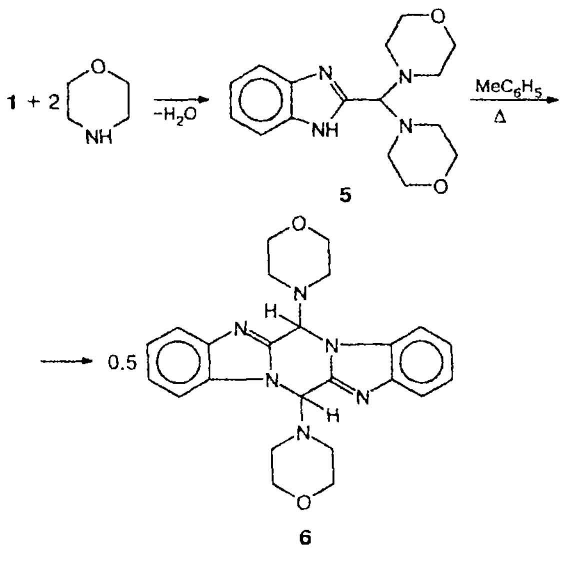
**Scheme 2**



*i*. 140—160 °C, 10 min.

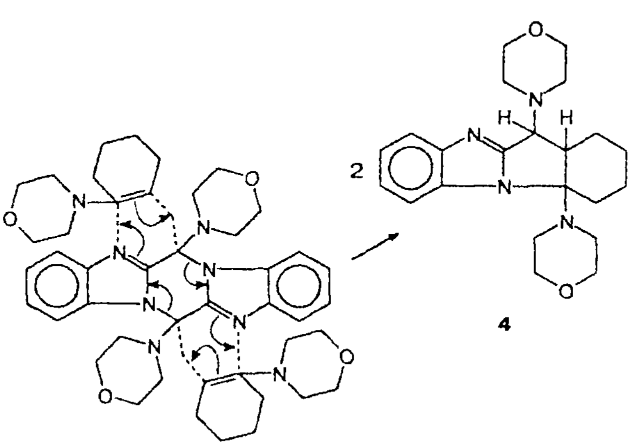
Cycloaddition was accompanied by the replacement of the hydroxyl groups with the morpholine fragments, *i.e.*, the enamine reacted with dimer **1** both as a dipolarophile and amine, the first stage involving apparently the replacement of the hydroxyl groups by the morpholine moieties. It should be noted that the reaction of **1** with morpholine (unlike other secondary amines) is a more complex process than that reported in Ref. 3. Heating of **1** with an excess of morpholine afforded poorly soluble product **5** with the stoichiometry of the normal aminal. Product **5**, while quite stable under normal conditions, readily lost the morpholine molecule upon heating in organic solvents (for example, in toluene) and was converted into product **6** described previously[3] (Scheme 3).

**Scheme 3**



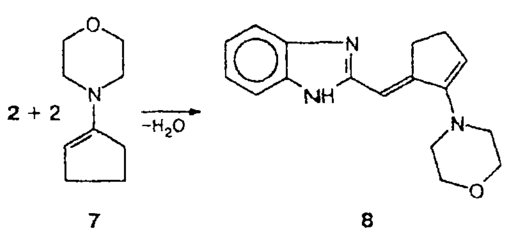
Heating of compound **6** with enamine **3** also gave compound **4**. The assumed mechanism of this interaction is shown in Scheme 4, which illustrates only the fact that cycloaddition can occur at the periphery of molecule **6** without its preliminary dissociation. In this case, the concerted reaction with the nonaromatic (the more so, with antiaromatic) transition state is not implied.

**Scheme 4**



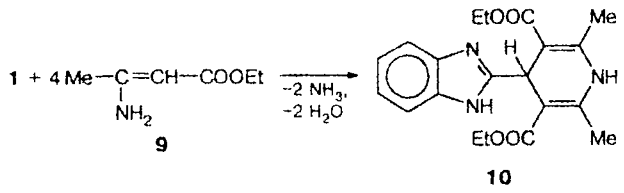
Under the same conditions, the reaction of 1-morpholinocyclopentene (**7**) with compound **1** yielded 2-(2-morpholino-4,5-dihydrofulvenyl)benzimidazole (**8**) (Scheme 5), *i.e.*, condensation, which is analogous to that reported for aliphatic and aromatic aldehydes, rather than 1,3-bipolar cycloaddition, occurred.[4]

**Scheme 5**



The reaction of **1** with aminocrotonic ester **9** [5] afforded 4-(benzimidazol-2-yl)-3,5-diethoxycarbonyl-2,6-dimethyl-1,4-dihydropyridine (**10**), *i.e.*, the product of the Hantzsch reaction[6] (Scheme 6). Under analogous conditions, compound **10** was formed also from morpholine derivative **6**.

Scheme 6



The structures of compounds **4** and **8** were established by X-ray diffraction analysis (Figs. 1 and 2; Tables 2—7). The benzimidazole fragment of molecule **4** and the C(13) and C(7) atoms attached to this fragment are in a single plane (to within 0.04 Å). The pyrroline ring adopts an envelope conformation. The C(8) atom of this ring deviates from the above-mentioned planar moiety by 0.15 Å. The cyclohexane and pyrroline rings are *cis*-fused (the H(8)—C(8)—C(13)—N(4) torsion angle is 15°). The C(11) atom of the cyclohexane fragment in the molecule is disordered over two sites with an occupancy ratio C(11)/C(11a) = 0.77/0.23 (see Fig. 1). The ring containing the C(11a) atom has a twist-boat conformation, while the ring containing the C(11) atom adopts a chair conformation. The puckering parameters are as follows: $S = 0.77$, $\theta = 82.5$, and $\psi = 22.2$ in the first case; $S = 1.0$, $\theta = 16.9$, and $\psi = 3.4$ in the second case.[7]

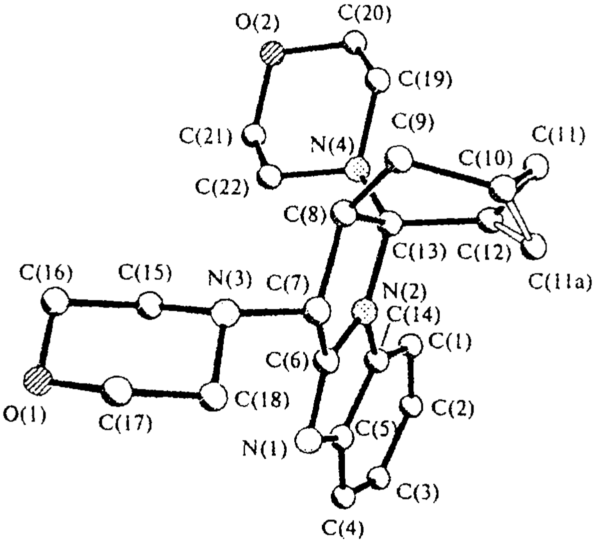


**Fig. 1.** Overall view of molecule **4**.

The environment about the C(13) atom is somewhat distorted, which is manifested in the elongation of the C(8)—C(13) bond (1.577(5) Å) compared to the stan-

**Table 2.** Coordinates (×10⁴) and equivalent isotropic thermal parameters (×10³/Å²) of nonhydrogen atoms in the structure of **4**

| Atom | x | *y* | *z* | $U_{eq}$ |
|---|---|---|---|---|
| O(1) | 9856(3) | 10739(3) | 969(2) | 74(1) |
| O(2) | 2912(2) | 13857(3) | 1320(2) | 72(1) |
| N(1) | 7702(3) | 9536(3) | 2870(2) | 57(1) |
| N(2) | 5676(3) | 9912(3) | 2395(1) | 43(1) |
| N(3) | 7586(3) | 9686(3) | 1182(2) | 51(1) |
| N(4) | 3960(2) | 11194(3) | 1739(2) | 45(1) |
| C(1) | 5004(4) | 10469(4) | 3515(2) | 52(1) |
| C(2) | 5504(4) | 10576(4) | 4233(2) | 60(1) |
| C(3) | 6770(5) | 10370(4) | 4528(2) | 65(1) |
| C(4) | 7579(4) | 10039(4) | 4117(2) | 64(1) |
| C(5) | 7107(3) | 9907(4) | 3398(2) | 48(1) |
| C(6) | 6790(3) | 9542(4) | 2293(2) | 45(1) |
| C(7) | 6673(3) | 9154(4) | 1542(2) | 45(1) |
| C(8) | 5333(3) | 9616(4) | 1180(2) | 44(1) |
| C(9) | 4692(4) | 8631(5) | 596(2) | 64(1) |
| C(10) | 4222(4) | 7315(5) | 870(2) | 74(1) |
| C(11) | 3243(5) | 7764(5) | 1234(2) | 66(1) |
| C(11A) | 4151(17) | 7280(9) | 1627(4) | 66(1) |
| C(12) | 3776(4) | 8653(4) | 1864(2) | 57(1) |
| C(13) | 4613(3) | 9862(4) | 1772(2) | 43(1) |
| C(14) | 5819(3) | 10124(4) | 3112(2) | 43(1) |
| C(15) | 7928(4) | 11130(4) | 1322(2) | 58(1) |
| C(16) | 8804(4) | 11580(5) | 872(3) | 74(1) |
| C(17) | 9512(4) | 9328(5) | 838(3) | 71(1) |
| C(18) | 8692(4) | 8847(5) | 1300(2) | 66(1) |
| C(19) | 2847(3) | 11347(5) | 1167(2) | 59(1) |
| C(20) | 2160(4) | 12644(4) | 1281(2) | 65(1) |
| C(21) | 4012(4) | 13701(4) | 1866(2) | 66(1) |
| C(22) | 4729(3) | 12434(3) | 1756(2) | 49(1) |

**Table 3.** Bond lengths (*d*) in the structure of **4**

| Bond | *d*/Å | Bond | *d*/Å | Bond | *d*/Å | Bond | *d*/Å |
|---|---|---|---|---|---|---|---|
| O(1)—C(16) | 1.394(5) | N(3)—C(18) | 1.439(5) | C(3)—C(4) | 1.381(6) | C(10)—C(11) | 1.500(5) |
| O(1)—C(17) | 1.421(5) | N(3)—C(15) | 1.453(5) | C(4)—C(5) | 1.383(5) | C(10)—C(11A) | 1.505(6) |
| O(2)—C(21) | 1.419(4) | N(3)—C(7) | 1.459(4) | C(5)—C(14) | 1.415(5) | C(11)—C(12) | 1.499(5) |
| O(2)—C(20) | 1.428(5) | N(4)—C(19) | 1.457(4) | C(6)—C(7) | 1.493(5) | C(11A)—C(12) | 1.496(6) |
| N(1)—C(6) | 1.320(4) | N(4)—C(22) | 1.464(4) | C(7)—C(8) | 1.547(5) | C(12)—C(13) | 1.528(5) |
| N(1)—C(5) | 1.401(5) | N(4)—C(13) | 1.468(4) | C(8)—C(9) | 1.523(5) | C(15)—C(16) | 1.524(6) |
| N(2)—C(6) | 1.345(5) | C(1)—C(14) | 1.377(5) | C(8)—C(13) | 1.577(5) | C(17)—C(18) | 1.502(6) |
| N(2)—C(14) | 1.390(4) | C(1)—C(2) | 1.384(5) | C(9)—C(10) | 1.519(6) | C(19)—C(20) | 1.509(6) |
| N(2)—C(13) | 1.476(4) | C(2)—C(3) | 1.395(6) | | | C(21)—C(22) | 1.502(5) |

**Table 4.** Bond angles (ω) in the structure of **4**

| Angle | ω/deg | Angle | ω/deg | Angle | ω/deg |
|---|---|---|---|---|---|
| C(16)—O(1)—C(17) | 110.7(3) | N(1)—C(5)—C(14) | 110.9(3) | N(4)—C(13)—C(12) | 111.5(3) |
| C(21)—O(2)—C(20) | 109.6(3) | N(1)—C(6)—N(2) | 114.3(3) | N(2)—C(13)—C(12) | 108.2(3) |
| C(6)—N(1)—C(5) | 103.3(3) | N(1)—C(6)—C(7) | 135.0(3) | N(4)—C(13)—C(8) | 115.6(3) |
| C(6)—N(2)—C(14) | 107.9(3) | N(2)—C(6)—C(7) | 110.6(3) | N(2)—C(13)—C(8) | 99.7(2) |
| C(6)—N(2)—C(13) | 116.4(3) | N(3)—C(7)—C(6) | 119.0(3) | C(12)—C(13)—C(8) | 113.7(3) |
| C(14)—N(2)—C(13) | 135.3(3) | N(3)—C(7)—C(8) | 112.2(3) | C(1)—C(14)—N(2) | 133.3(3) |
| C(18)—N(3)—C(15) | 109.6(3) | C(6)—C(7)—C(8) | 102.8(3) | C(1)—C(14)—C(5) | 123.2(3) |
| C(18)—N(3)—C(7) | 112.8(3) | C(9)—C(8)—C(7) | 112.5(3) | N(2)—C(14)—C(5) | 103.4(3) |
| C(15)—N(3)—C(7) | 115.2(3) | C(9)—C(8)—C(13) | 114.8(3) | N(3)—C(15)—C(16) | 109.7(3) |
| C(19)—N(4)—C(22) | 108.2(3) | C(7)—C(8)—C(13) | 107.9(2) | O(1)—C(16)—C(15) | 112.6(4) |
| C(19)—N(4)—C(13) | 115.9(3) | C(10)—C(9)—C(8) | 113.1(3) | O(1)—C(17)—C(18) | 111.2(4) |
| C(22)—N(4)—C(13) | 115.9(3) | C(11)—C(10)—C(9) | 106.1(4) | N(3)—C(18)—C(17) | 110.2(4) |
| C(14)—C(1)—C(2) | 116.4(4) | C(11A)—C(10)—C(9) | 118.2(6) | N(4)—C(19)—C(20) | 109.4(3) |
| C(1)—C(2)—C(3) | 121.5(4) | C(12)—C(11)—C(10) | 111.8(4) | O(2)—C(20)—C(19) | 112.2(3) |
| C(4)—C(3)—C(2) | 121.5(4) | C(12)—C(11A)—C(10) | 111.8(5) | O(2)—C(21)—C(22) | 111.4(3) |
| C(3)—C(4)—C(5) | 118.5(4) | C(11A)—C(12)—C(13) | 114.6(7) | N(4)—C(22)—C(21) | 110.1(3) |
| C(4)—C(5)—N(1) | 130.1(4) | C(11)—C(12)—C(13) | 117.9(3) | | |
| C(4)—C(5)—C(14) | 118.9(3) | N(4)—C(13)—N(2) | 107.0(3) | | |

**Table 5.** Coordinates of nonhydrogen atoms (×10$^4$) and hydrogen atoms (×10$^3$) and their equivalent isotropic thermal parameters (×10$^3$/Å) in the structure of **8**

| Atom | *x* | *y* | *z* | $U_{eq}$ | Atom | *x* | *y* | *z* | $U_{eq}$ |
|---|---|---|---|---|---|---|---|---|---|
| O(1) | 1938(1) | 5764(1) | 5688(1) | 27(1) | C(17) | 2159(2) | 4880(1) | 4327(1) | 23(1) |
| N(1) | 6879(1) | 4549(1) | 2612(1) | 20(1) | H(1N) | 729(2) | 446(2) | 312(1) | 45(5) |
| N(2) | 5345(1) | 5101(1) | 1469(1) | 20(1) | H(3) | 651(2) | 457(2) | −2(1) | 45(5) |
| N(3) | 2151(1) | 6238(1) | 3998(1) | 19(1) | H(4) | 899(2) | 364(2) | −6(1) | 34(4) |
| C(1) | 5487(1) | 5067(1) | 2285(1) | 19(1) | H(5) | 1057(2) | 298(2) | 111(1) | 35(4) |
| C(2) | 6715(1) | 4563(1) | 1260(1) | 19(1) | H(6) | 977(2) | 334(2) | 245(1) | 42(5) |
| C(3) | 7203(2) | 4345(1) | 484(1) | 23(1) | H(8) | 463(2) | 542(2) | 340(1) | 42(5) |
| C(4) | 8639(2) | 3773(1) | 454(1) | 26(1) | H(10B) | 209(2) | 532(2) | 140(1) | 30(4) |
| C(5) | 9579(2) | 3400(1) | 1166(1) | 25(1) | H(10A) | 287(2) | 668(2) | 140(1) | 43(5) |
| C(6) | 9115(2) | 3606(1) | 1938(1) | 24(1) | H(11B) | −22(2) | 629(2) | 154(1) | 35(4) |
| C(7) | 7684(1) | 4203(1) | 1967(1) | 19(1) | H(11A) | 60(2) | 771(2) | 159(1) | 35(5) |
| C(8) | 4355(1) | 5468(1) | 2819(1) | 19(1) | H(12) | −38(2) | 715(2) | 293(1) | 35(4) |
| C(9) | 2922(1) | 5907(1) | 2582(1) | 18(1) | H(14B) | 121(2) | 799(2) | 428(1) | 33(4) |
| C(10) | 2187(2) | 6141(1) | 1718(1) | 24(1) | H(14A) | 11(2) | 674(2) | 444(1) | 30(4) |
| C(11) | 618(2) | 6804(1) | 1810(1) | 23(1) | H(15B) | 294(2) | 746(2) | 541(1) | 38(5) |
| C(12) | 524(2) | 6818(1) | 2715(1) | 23(1) | H(15A) | 121(2) | 761(2) | 570(1) | 30(4) |
| C(13) | 1795(1) | 6313(1) | 3138(1) | 18(1) | H(16B) | 395(2) | 523(2) | 525(1) | 31(4) |
| C(14) | 1194(2) | 7079(1) | 4467(1) | 24(1) | H(16A) | 282(2) | 404(2) | 546(1) | 46(5) |
| C(15) | 1872(2) | 7082(1) | 5354(1) | 29(1) | H(17B) | 110(2) | 452(2) | 428(1) | 24(4) |
| C(16) | 2819(2) | 4913(2) | 5219(1) | 29(1) | H(17A) | 283(2) | 428(2) | 399(1) | 33(4) |

**Table 6.** Bond lengths (*d*) in the structure of **8**

| Bond | *d*/Å | Bond | *d*/Å | Bond | *d*/Å | Bond | *d*/Å |
|---|---|---|---|---|---|---|---|
| O(1)—C(16) | 1.429(2) | N(3)—C(13) | 1.4150(14) | C(3)—C(4) | 1.380(2) | C(9)—C(10) | 1.509(2) |
| O(1)—C(15) | 1.434(2) | N(3)—C(14) | 1.462(2) | C(4)—C(5) | 1.402(2) | C(10)—C(11) | 1.540(2) |
| N(1)—C(1) | 1.372(2) | N(3)—C(17) | 1.469(2) | C(5)—C(6) | 1.386(2) | C(11)—C(12) | 1.498(2) |
| N(1)—C(7) | 1.376(2) | C(1)—C(8) | 1.444(2) | C(6)—C(7) | 1.387(2) | C(12)—C(13) | 1.339(2) |
| N(2)—C(1) | 1.3309(14) | C(2)—C(3) | 1.403(2) | C(8)—C(9) | 1.339(2) | C(14)—C(15) | 1.510(2) |
| N(2)—C(2) | 1.384(2) | C(2)—C(7) | 1.406(2) | C(9)—C(13) | 1.467(2) | C(16)—C(17) | 1.513(2) |

dard value (1.532 Å),[8] apparently due to shortened intramolecular contacts in molecule **4**: H(8)...H(22a), 2.14 Å; H(19a)...H(12b), 2.26 Å; and H(19a)...H(12d), 1.88 Å (the normal H...H distance is 2.31 Å).[9] The two last-mentioned contacts characterize the chair and twist-boat conformations of the cyclohexane ring, respec-

**Table 7.** Bond angles (ω) in the structure of **8**

| Angle | ω/deg | Angle | ω/deg | Angle | ω/deg |
|---|---|---|---|---|---|
| C(16)—O(1)—C(15) | 110.47(10) | C(3)—C(8)—C(7) | 119.73(11) | C(13)—C(9)—C(10) | 107.29(10) |
| C(1)—N(1)—C(7) | 107.14(10) | C(4)—C(3)—C(2) | 117.45(11) | C(9)—C(10)—C(11) | 105.42(10) |
| C(1)—N(2)—C(2) | 104.52(10) | C(3)—C(4)—C(5) | 121.98(11) | C(12)—C(11)—C(10) | 104.15(10) |
| C(13)—N(3)—C(14) | 114.80(10) | C(6)—C(5)—C(4) | 121.38(12) | C(13)—C(12)—C(11) | 112.34(11) |
| C(13)—N(3)—C(17) | 114.10(9) | C(5)—C(6)—C(7) | 116.55(11) | C(12)—C(13)—N(3) | 128.04(11) |
| C(14)—N(3)—C(17) | 108.99(9) | N(1)—C(7)—C(6) | 132.00(11) | C(12)—C(13)—C(9) | 110.63(10) |
| N(2)—C(1)—N(1) | 112.68(10) | N(1)—C(7)—C(2) | 105.10(10) | N(3)—C(13)—C(9) | 121.16(10) |
| N(2)—C(1)—C(8) | 127.45(11) | C(6)—C(7)—C(2) | 122.89(11) | N(3)—C(14)—C(15) | 108.92(10) |
| N(1)—C(1)—C(8) | 110.04(10) | C(9)—C(8)—C(1) | 126.08(10) | O(1)—C(15)—C(14) | 111.22(11) |
| N(2)—C(2)—C(3) | 129.72(11) | C(8)—C(9)—C(13) | 125.01(10) | O(1)—C(16)—C(17) | 111.43(11) |
| N(2)—C(2)—C(7) | 110.55(10) | C(8)—C(9)—C(10) | 127.64(11) | N(3)—C(17)—C(16) | 108.75(10) |

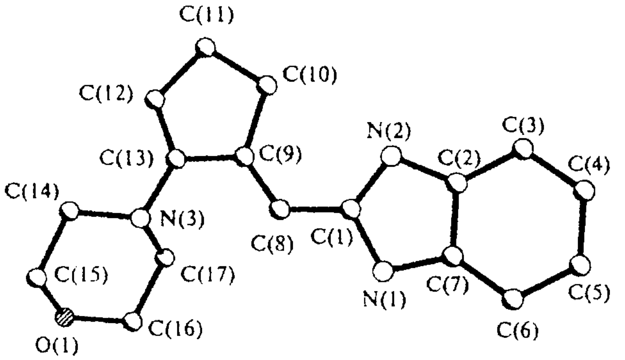


**Fig. 2.** Overall view of molecule **8**.

tively, and indicate that the twist-boat conformation is more strained.

Both morpholine rings in the molecule adopt a chair conformation. The O(1) and N(3) atoms at the C(7) atom of the morpholine ring deviate from the plane through the carbon atoms (the root-mean-square (rms) deviation of the atoms from the plane is 0.011 Å) by 0.62 and −0.66 Å, respectively. The corresponding deviations of the O(2) and N(4) atoms at the C(13) atom of the morpholine ring (the rms deviation for the plane through the C(19)...C(22) atoms is 0.003 Å) are 0.64 and −0.69 Å, respectively.

In the crystal of **4**, no shortened intermolecular contacts are observed.

In molecule **8**, the five-membered C(9)...C(13) ring adopts an envelope conformation. The deviation of the C(10) atom from the plane through the remaining atoms of the ring is −0.06 Å. Apparently, the nonplanar conformation of this ring is realized due to the presence of the shortened intramolecular contacts N(2)...C(10) (3.01 Å; the sum of the van der Waals radii[9] is 3.21 Å).

The N(3)...C(17) morpholine ring has a chair conformation. The deviations of the N(3) and O(1) atoms from the rms plane through the remaining atoms of the ring are 0.70 Å and −0.64 Å, respectively. Apparently, this conformation of the ring is responsible for the following shortened intramolecular contacts: N(3)...H(8), 2.60 Å (2.66 Å); C(8)...C(17), 3.34 Å (3.42 Å); C(8)...H(17A), 2.37 Å (2.87 Å); H(8)...C(17), 2.82 Å; H(8)...H(17A), 2.24 Å (2.32 Å); C(9)...H(17A), 2.84 Å; C(12)...H(14B), 2.83 Å; and H(12)...C(14), 2.74 Å.

In the crystal of **8**, molecules are linked in dimers through intermolecular N—H...O hydrogen bonds between the hydrogen atom of the imidazole ring and the oxygen atom of the morpholine ring (H(1N)...O(1) (1−*x*, 1−*y*, 1−*z*), 2.02(2) Å; N(1)...O(1), 2.884(2) Å; the N(1)—H(1N)...O(1) angle is 175(2)°).

## Experimental

The IR spectra were recorded on a Specord IR-75 instrument as Nujol mulls. The $^1$H NMR spectra were obtained on a Unity-300 spectrometer.

**4a,11-Dimorpholino-1,2,3,4,11,11a-hexahydro-4a*H*-indolo[1,2-*a*]benzimidazole (4).** *A.* A mixture of aldehyde **1** (1.46 g, 0.005 mol), which had been ground in a mortar, and 1-morpholinocyclohexene (**3**) (3.5 mL, 0.02 mol) was heated until the exothermic reaction started (~120 °C). The temperature increased to 155—160 °C. The reaction mixture was kept at this temperature for 10 min and then cooled. Then toluene (2 mL) and isooctane (10 mL) were added. The adhesive crystalline compound that formed was transferred to a filter, washed with cold propan-2-ol and MeOH, and dried. The yield was 1.8 g (47%).

*B.* Heating of morpholine derivative **6** with an excess of enamine **3** (25%) at 170 °C for 10 min afforded the same compound in a yield of ~50%.

Compound **4** is a colorless compound that crystallizes from MeOH. It has no distinct melting temperature. Compound **4** turned dark above 190 °C and melted with decomposition at about 270 °C. Found (%): C, 69.06; H, 7.61; N, 14.36. $C_{22}H_{30}N_4O_2$. Calculated (%): C, 69.08; H, 7.91; N, 14.65. IR, ν/cm$^{-1}$: 1614, 1514 (arom.), 1114 (C—O—C), 754 (C—H, arom., deform.). $^1$H NMR (CDCl$_3$), δ: 1.16—1.96 (m, 7 H, CH); 2.30 (m, 1 H, CH); 2.57 (dd, 2 H, $CH_2N$, *J* = 4.7 Hz); 2.75 (dd, 2 H, $CH_2N$, *J* = 4.7 Hz); 2.96 (dd, 2 H, $CH_2N$, *J* = 9.4 Hz); 3.06 (dd, 2 H, $CH_2N$, *J* = 4.7 Hz); 3.71 (t, 4 H, $CH_2O$, *J* = 4.7 Hz); 3.73 (t, 4 H, $CH_2O$, *J* = 4.7 Hz); 3.83 (d, 1 H, C(11)H, *J* = 7.3 Hz); 7.20 (m, 2 H, C(7)H+C(8)H); 7.55 (dd, 1 H, CH, *J* = 7 Hz); 7.73 (dd, 1 H, CH, *J* = 7 Hz).

**2-(2-Morpholino-4,5-dihydrofulvenyl)benzimidazole (8).** A mixture of aldehyde **1** (1 g, 0.034 mol), which had been ground in a mortar, and 1-morpholinocyclopentene (7) (2.5 mL, 0.015 mol) was heated until the exothermic reaction started (~120 °C). After completion of the reaction (1—2 min), *o*-xylene (10 mL) was added to the hot solution and the mixture was cooled to ~20 °C. The precipitate that formed was filtered off, washed with *o*-xylene and hexane, and dried. The crude product was obtained in quantitative yield. Recrystallization from propan-2-ol afforded pale-yellowish crystals in a yield of 0.75 g (78%), m.p. 215—217 °C. Found (%): C, 72.67; H, 6.50; N, 14.26. $C_{17}H_{19}N_3O$. Calculated (%): C, 72.57; H, 6.81; N, 14.93. IR, $\nu$/cm$^{-1}$: 1641, 1614, 1594, 1527 (C=C, arom.); 1107 (C—O—C). $^1$H NMR (CDCl$_3$), $\delta$: 2.55 (m, 2 H, CH$_2$); 2.87 (t, 4 H, CH$_2$N, $J$ = 4.7 Hz); 3.16 (m, 2 H, CH$_2$); 3.74 (t, 4 H, CH$_2$O, $J$ = 4.7 Hz); 5.64 (m, 1 H, =CH); 6.45 (s, 1 H, =CH); 7.20 (m, 2 H, C(5)H + C(6)H); 7.55 (m, 2 H, C(4)H + C(7)H).

**4-(Benzimidazol-2-yl)-3,5-diethoxycarbonyl-2,6-dimethyl-1,4-dihydropyridine (10).** *A.* A mixture of aldehyde **1** (0.29 g, 0.001 mol), which had been ground in a mortar, and aminocrotonic ester **9** (1 mL, ~0.008 mol) was boiled for 3 min and cooled. Then MeOH (3 mL) was added and the precipitate that formed was filtered off, washed with MeOH, and dried. The yield of the crude product was 0.23 g (62%).

*B.* A mixture of morpholine derivative **6** (0.26 g, 0.0006 mol) and aminocrotonic ester **9** (0.5 mL, ~0.004 mol) was heated at 140 °C for 2 min and cooled. Then MeOH (3 mL) was added and the mixture was filtered, washed with MeOH, and dried. The yield of the crude product was 0.22 g (quantitative).

Compound **10** is a colorless compound soluble in DMSO, DMF, and propylene carbonate upon heating; m.p. 280—283 °C (from propylene carbonate). Found (%): C, 65.24; H, 6.44; N, 11.68. $C_{20}H_{23}N_3O_4$. Calculated (%): C, 65.03; H, 6.28; N, 11.37. IR, $\nu$/cm$^{-1}$: 3326, 3273, 3167 (NH), 1700 (CO), 1647, 1634, 1600, 1500 (C=C, arom.). $^1$H NMR (DMSO-d$_6$), $\delta$: 1.11 (t, 6 H, CH$_3$, $J$ = 7 Hz); 2.25 (s, 6 H, CH$_3$); 4.03 (q, 4 H, CH$_2$, $J$ = 7 Hz); 5.13 (s, 1 H, C(2)H); 7.04 (m, 2 H, C(5)H + C(6)H); 7.41 (m, 2 H, C(4)H + C(7)H); 8.98 (s, 1 H, NH); 11.61 (s, 1 H, NH).

### X-ray diffraction study of compounds 4 and 8

**Compound 4.** Crystals of **4** are monoclinic, at 20 °C $a$ = 11.0776(14), $b$ = 9.6464(12), $c$ = 19.585(3) Å, $\beta$ = 104.12(1)°, $V$ = 2029.6(5) Å$^3$, $Z$ = 4, space group $P2_1/n$, $d_{calc}$ = 1.252 g cm$^{-3}$, $\mu$(Cu-K$\alpha$) = 0.650 mm$^{-1}$, $F$(000) = 824. The unit cell parameters and intensities of 2529 reflections were measured on an automated four-circle Siemens P3/PC diffractometer ($\lambda$ Cu-K$\alpha$ radiation, $\beta$ filter, 2$\theta$/$\theta$ scanning technique, 2$\theta_{max}$ = 140°). The structure was solved by the direct method using the SHELXTL PLUS program package.[10] The positions of the hydrogen atoms were calculated geometrically and refined using the riding model with $U_{iso}$ = 1.2$U_{eq}$ of the nonhydrogen atoms to which the hydrogen atoms are attached. The disordered C(11) and C(11a) atoms were refined using the following geometrical restrictions: the equality of the C(10)—C(11), C(10)—C(11a), C(12)—C(11), and C(12)—C(11a) bonds to within 0.005 Å and the equality of the components $U_{ij}$ of anisotropic thermal vibrations. The structure was refined anisotropically by the full-matrix least-squares method based on $F^2$ to $wR_2$ = 0.2027 using 2258 reflections ($R_1$ = 0.071 using 1813 reflections with $F > 4\sigma(F)$, $S$ = 1.082).

**Compound 8.** Crystals of **8** are monoclinic, at 193(2) K $a$ = 8.691(3), $b$ = 10.066(3), $c$ = 16.413(6) Å, $\beta$ = 96.21(3)°, $V$ = 1427.3(9) Å$^3$, crystal dimensions 0.5×0.4×0.3 mm, space group $P2_1/n$, $Z$ = 4, $d_{calc}$ = 1.309 g cm$^{-3}$, $F$(000) = 600, $\mu$ = 0.084 mm$^{-1}$.

Intensities of 4020 reflections (3786 independent reflections, $R_{int}$ = 0.028) were measured on an automated four-circle Syntex P2$_1$/PC diffractometer (graphite monochromator, Mo-K$\alpha$ radiation, $\theta$/2$\theta$ scanning technique, 2$\theta_{max}$ = 58°). The structure was solved by the direct method with the use of the SHELXTL PLUS program package.[10] The positions of the hydrogen atoms were located from the difference electron density synthesis. The refinement by the full-matrix least-squares method based on $F^2$ with anisotropic thermal parameters for nonhydrogen atoms and isotropic thermal parameters for hydrogen atoms (266 parameters) using 3724 reflections converged to $R_1$ = 0.050 (for 2877 reflections with $F > 4\sigma(F)$), $wR_2$ = 0.136, $S$ = 0.96.

This work was financially supported by the Russian Foundation for Basic Research (Project Nos. 97-032894a and 97-03-33783) and by the Program "Leading Scientific Schools" (Project No. 96-15-97367).

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*Received April 27, 1998;*
*in revised form June 25, 1998*