Molecular structure and conformational dynamics of 3,12-dichloro-5,14-diphenyl-7,9a,16,18a-tetrazadibenzo[*a*,*l*]pentacene-9,18-dione

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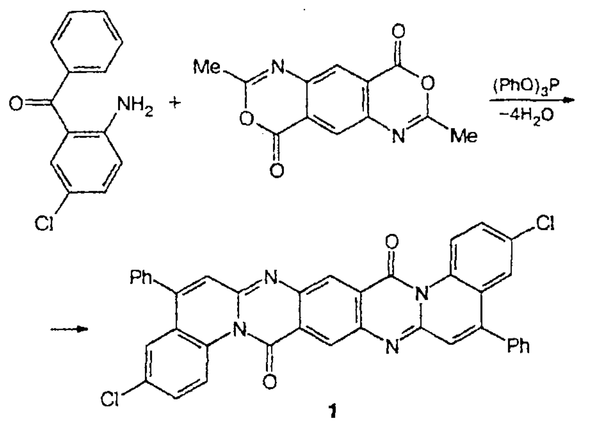
The X-ray study of 3,12-dichloro-5,14-diphenyl-7,9a,16,18a-tetrazadibenzo[*a*,*l*]pentacene-9,18-dione (**1**), a model compound for a novel class of thermostable polyheteroarylenes, polyquinoquinazolones, has been carried out. The nonsymmetric flattened structure of the molecule observed is a result of intermolecular interactions. It was established using quantum-chemical calculations by the semiempirical AM1 method that the annelation of the 1,6-dihydropyrimidinone ring by aromatic cycles results in increasing the conformational flexibility of the dihydrocycle due to weakening the conjugation between the carbonyl group and the remaining π-system of the molecule. It was shown by X-ray study and quantum-chemical calculations that protonation of **1** results in a substantial change in the molecular structure due to the large contribution of the 1,4-dihydro tautomeric form to the structure of the 1,6-dihydropyrimidinone ring. A tendency for the conformational flexibility of the heterocycle to increase upon protonation was revealed.

Key words: molecular structure, conformational analysis, 5,14-diphenyl-3,12-dichloro-7,9a,16,18a-tetrazadibenzo[*a*,*l*]pentacene-9,18-dione, AM1.

Previously,[1] we have synthesized a novel class of thermostable heterocyclic polymers, polyquinoquinazolones, based on bis-benzoxazines and bis-*o*-aminobenzophenones.

A model compound **1** was synthesized in the reaction



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and its crystal structure was studied to investigate conformational, spectral, and thermal properties and the "structure—properties" relationship of polymers of such type. The reaction of 2-amino-5-chlorobenzophenone with 2,2′-dimethyl-bis-benzoxazinone was carried out in a triphenyl phosphate medium over a period of 8 h at 140 °C following the procedure described in Ref. 1. The product precipitated in the course of synthesis was isolated in ~80% yield by simple filtration. An adduct of compound **1** with CF_3COOH (compound **2**) was also obtained and its structure was studied by X-ray method. The results of X-ray studies of related compounds (**3** and **4**) and those of our quantum-chemical calculations of model systems **5**—**22** were used in the discussion.

Experimental

X-ray study. The crystals of compound **1** ($C_{38}H_{20}Cl_2N_4O_2$) were obtained by evaporation of its solution in *N*-methylpyrrolidone. The parameters of the triclinic cell obtained at −80 °C are a = 8.017(3) Å, b = 10.976(5) Å, c = 16.207(6) Å, α = 96.38(3)°, β = 95.08(3)°, γ = 101.17(3)°, V = 1381.5(9) Å^3, space group $P\bar{1}$, Z = 2, d_{calc} = 1.528 g cm^{-3}, and μ = 0.282 mm^{-1}. The intensities of 6847 reflections (6390 independent reflections, R_{int} = 0.077) were measured on an automatic four-circle Syntex P2$_1$/PC diffractometer (graphite monochromator, Mo-Kα radiation, θ/2θ scan, $2\theta_{max}$ = 55°). The structure was solved by direct methods using the SHELXTL PLUS 5 program package.[2] Positions of hydrogen atoms were located from the difference electron density synthesis and refined using the riding model without fixing U_{iso} values. The full-matrix LSM F^2-refinement in anisotropic approximation for nonhydrogen atoms using 6307 reflections was conducted to R_1 = 0.076 (for 3329 reflections with $F > 4\sigma(F)$), wR_2 = 0.15, and S = 1.009. The atomic coordinates are listed in Table 1, and the bond lengths and bond angles are given in Tables 2 and 3.

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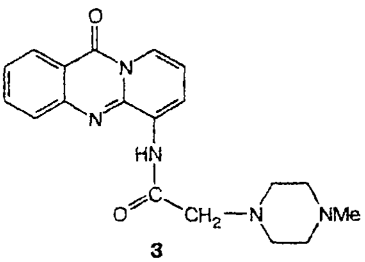
Crystals of compound $C_{38}H_{22}Cl_2N_4O_2{}^{2+} \cdot 2(CF_3COO^-)$ (**2**) are monoclinic. The cell parameters obtained at −86 °C are a = 21.103(2) Å, b = 30.039(3) Å, c = 7.891(4) Å, β = 100.31(1)°, V = 4978(4) Å^3, space group $C2/c$, Z = 4, d_{calc} = 1.5 g cm^{-3}, and μ = 0.260 mm^{-1}. The intensities of 4378 reflections (4159 independent reflections, R_{int} = 0.1046) were measured on an automatic four-circle Syntex P2$_1$/PC diffractometer (graphite monochromator, Mo-Kα radiation, θ/2θ scan, $2\theta_{max}$ = 50°). The structure was solved by direct methods using the SHELXTL PLUS 4.2 program package.[3] Positions of hydrogen atoms were calculated geometrically (except for the H(4) atom whose position was located from the difference electron density synthesis) and refined using the riding model with a fixed U_{iso} = 0.03 Å^2. The full-matrix LSM F-refinement in anisotropic approximation for nonhydrogen atoms using 1808 reflections with $F > 7\sigma(F)$ was conducted to R = 0.096, R_w = 0.115, and S = 2.52. The atomic coordinates are listed in Table 4, and the bond lengths and bond angles are given in Tables 5 and 6.

Quantum-chemical calculations. The spatial structures of compounds **5**—**22** were calculated by the semiempirical quantum-chemical AM1 method[4] with full optimization of geometry. The conformational flexibility of 1,6-dihydropyrimidine cycle was studied by scanning the =C—NH—C(=O)—C= torsion angle in the ±30° interval with an increment of 10°. For compounds **11**—**13** and **20**—**22**, symmetric and antisymmetric changes in the above torsion angles in two dihydrocycles were considered. The results of calculations are listed in Tables 7 and 8.

Preparation of a crystal solvate of compound 1 (compound 2). Compound **1** was dissolved in a mixture of trifluoroacetic and 85% formic acid (2 : 1 by volume) with heating and then allowed to stay for 10 days at −20 °C. The air-unstable crystals of **2** that formed were filtered off, dried, and used in the X-ray study. In the air, crystals of **2** lose the formic acid and water molecules to be converted into a powdered salt **1** · 2CF$_3$COOH, which decomposes without melting at temperatures above 250 °C. Found (%): C, 59.00; H, 2.65; N, 7.52; Cl, 8.12; F, 13.14. $C_{38}H_{20}Cl_2N_4O_2 \cdot 2CF_3COOH$. Calculated (%): C, 58.86; H, 2.52; N, 7.34; Cl, 8.15; F, 13.09.

Results and Discussion

Molecule **1** (Fig. 1) is asymmetric in the crystal. One of the dihydropyrimidinone cycles has the conformation of a flattened sofa (the C(7) atom deviates from the plane of the rest of atoms of the cycle by −0.08 Å), while the other cycle is planar, similarly to both dihydropyridine cycles. Previously,[5,6] the same distinction in the conformation of this dihydrocycle was revealed when comparing compounds **3** and **4**. The dihydropyrimidinone cycle in **3** is planar, whereas it has the conformation of a very flattened sofa in compound **4**.



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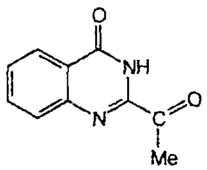

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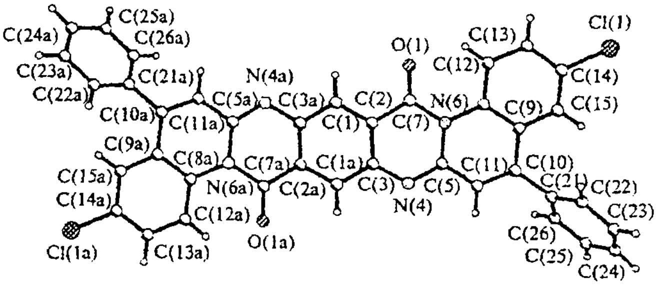


Fig. 1. The structure of compound **1**.

Table 1. Coordinates (×10^4) and equivalent isotropic thermal parameters (U_{eq}×10^3) of nonhydrogen atoms in structure **1**

Atom	x	y	z	U_{eq}/Å^2
Cl(1)	−4410(1)	742(1)	7514(1)	33(1)
O(1)	−2757(3)	4948(2)	4889(1)	35(1)
C(1)	−1223(4)	7200(3)	4398(2)	23(1)
C(2)	−637(4)	6782(3)	5124(2)	19(1)
C(3)	849(4)	7474(3)	5635(2)	20(1)
N(4)	1396(3)	7075(2)	6367(2)	22(1)
C(5)	531(3)	6056(3)	6590(2)	19(1)
N(6)	−990(3)	5293(2)	6140(1)	19(1)
C(7)	−1565(4)	5608(3)	5353(2)	21(1)
C(8)	−1831(4)	4199(3)	6464(2)	20(1)
C(9)	−1093(3)	3845(3)	7203(2)	19(1)
C(10)	472(4)	4626(3)	7650(2)	19(1)
C(11)	1175(4)	5682(3)	7356(2)	22(1)
C(12)	−3420(4)	3470(3)	6082(2)	23(1)
C(13)	−4203(4)	2423(3)	6400(2)	26(1)
C(14)	−3436(4)	2075(3)	7113(2)	24(1)
C(15)	−1921(4)	2788(3)	7516(2)	23(1)
C(21)	1305(3)	4274(3)	8434(2)	23(1)
C(22)	1966(4)	3195(3)	8410(2)	26(1)
C(23)	2849(4)	2924(3)	9116(2)	32(1)
C(24)	3074(4)	3732(3)	9852(2)	33(1)
C(25)	2400(4)	4799(3)	9890(2)	32(1)
C(26)	1541(4)	5082(3)	9181(2)	28(1)
Cl(1A)	4662(1)	14927(1)	2091(1)	28(1)
C(1A)	1764(4)	8550(3)	5375(2)	21(1)
O(1A)	3467(3)	10694(2)	4755(1)	37(1)
C(2A)	1178(4)	8973(3)	4641(2)	19(1)
C(3A)	−358(4)	8300(3)	4160(2)	21(1)
N(4A)	−985(3)	8710(2)	3448(2)	24(1)
C(5A)	−143(4)	9716(3)	3208(2)	21(1)
N(6A)	1430(3)	10453(2)	3607(1)	19(1)
C(7A)	2151(4)	10097(3)	4369(2)	23(1)
C(8A)	2237(4)	11527(3)	3251(2)	20(1)
C(9A)	1450(3)	11815(3)	2492(2)	19(1)
C(10A)	−172(4)	11054(3)	2092(2)	23(1)
C(11A)	−876(4)	10081(3)	2460(2)	25(1)
C(12A)	3759(4)	12326(3)	3623(2)	26(1)
C(13A)	4498(4)	13370(3)	3269(2)	25(1)
C(14A)	3730(4)	13625(3)	2537(2)	22(1)
C(15A)	2230(4)	12874(3)	2148(2)	21(1)
C(21A)	−1102(4)	11315(3)	1313(2)	24(1)
C(22A)	−348(4)	11395(3)	570(2)	31(1)
C(23A)	−1314(5)	11534(3)	−155(2)	40(1)
C(24A)	−3010(5)	11625(3)	−138(2)	43(1)
C(25A)	−3757(4)	11550(3)	591(2)	38(1)
C(26A)	−2811(4)	11403(3)	1318(2)	30(1)

Table 2. Bond lengths (*d*) in structure **1**

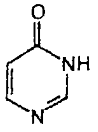
Bond	*d*/Å	Bond	*d*/Å
Cl(1)—C(14)	1.741(3)	C(25)—C(26)	1.384(4)
O(1)—C(7)	1.219(3)	Cl(1A)—C(14A)	1.742(3)
C(1)—C(3A)	1.383(4)	C(1A)—C(2A)	1.400(4)
C(1)—C(2)	1.386(4)	O(1A)—C(7A)	1.207(3)
C(2)—C(3)	1.420(4)	C(2A)—C(3A)	1.420(4)
C(2)—C(7)	1.461(4)	C(2A)—C(7A)	1.461(4)
C(3)—N(4)	1.376(4)	C(3A)—N(4A)	1.374(4)
C(3)—C(1A)	1.393(4)	N(4A)—C(5A)	1.296(4)
N(4)—C(5)	1.302(4)	C(5A)—N(6A)	1.417(3)
C(5)—N(6)	1.425(4)	C(5A)—C(11A)	1.432(4)
C(5)—C(11)	1.434(4)	N(6A)—C(8A)	1.436(4)
N(6)—C(7)	1.420(4)	N(6A)—C(7A)	1.442(4)
N(6)—C(8)	1.435(4)	C(8A)—C(12A)	1.400(4)
C(8)—C(12)	1.414(4)	C(8A)—C(9A)	1.427(4)
C(8)—C(9)	1.415(4)	C(9A)—C(15A)	1.406(4)
C(9)—C(15)	1.391(4)	C(9A)—C(10A)	1.455(4)
C(9)—C(10)	1.456(4)	C(10A)—C(11A)	1.335(4)
C(10)—C(11)	1.344(4)	C(10A)—C(21A)	1.493(4)
C(10)—C(21)	1.506(4)	C(12A)—C(13A)	1.391(4)
C(12)—C(13)	1.375(4)	C(13A)—C(14A)	1.370(4)
C(13)—C(14)	1.387(4)	C(14A)—C(15A)	1.374(4)
C(14)—C(15)	1.375(4)	C(21A)—C(26A)	1.392(4)
C(21)—C(22)	1.386(4)	C(21A)—C(22A)	1.398(4)
C(21)—C(26)	1.393(4)	C(22A)—C(23A)	1.389(4)
C(22)—C(23)	1.384(4)	C(23A)—C(24A)	1.385(5)
C(23)—C(24)	1.380(4)	C(24A)—C(25A)	1.375(5)
C(24)—C(25)	1.379(5)	C(25A)—C(26A)	1.387(4)

The shortened H(12)...O(1) [2.03 Å] and H(12A)...O(1A) [2.03 Å] intramolecular contacts (the sum of the van der Vaals radii^7 is equal to 2.45 Å) attract particular attention. The shortened intramolecular H...O contacts can be considered as hydrogen bonds (with the C—H...O angles of 124.2° and 126.2°, respectively), which must stabilize the planar molecular conformation. However, it has been shown previously$^{8-10}$ that shortened C(12)...O(1) [2.68 Å] (2.87 Å) and C(12A)...O(1a) [2.70 Å] intramolecular contacts having a strong repulsive character are also observed at these values of the C—H...O angles. As a result, the H...O contacts appear to be unfavorable and, hence, destabilize the planar conformation of the molecule.

The phenyl substituents C(21)...C(26) and C(21A)...C(26A) are rotated with respect to the C(10)—C(11) and C(10A)—C(11A) double bonds (the C(11)—C(10)—C(21)—C(26) and C(11A)—C(10A)—C(21A)—C(26A) torsion angles are equal to 59.0(4)° and 51.5(4)°, respectively), which is most likely due to the shortened H(15)...C(22) [2.68 Å] (the sum of the van der Vaals radii^7 is equal to 2.87 Å), H(11A)...C(26) [2.73 Å], and H(15A)...C(22A) [2.60 Å] intramolecular contacts. The shortened H(22)...N(4A)′ ($-x$, $1-y$, $1-z$) [2.46 Å] (2.66 Å), Cl(1)...H(11A)′ ($-1-x$, $1-y$, $1-z$) [2.95 Å] (3.06 Å), Cl(1)...C(8A)′ ($-x$, $1-y$, $1-z$) [3.49 Å] (3.61 Å), Cl(1)...H(26A)′ ($-1-x$, $1-y$, $1-z$) [3.01 Å],

Table 3. Bond angles (ω) in structure **1**

Angle	ω/deg	Angle	ω/deg	Angle	ω/deg
C(3A)—C(1)—C(2)	120.2(3)	C(12)—C(13)—C(14)	119.7(3)	O(1A)—C(7A)—N(6A)	122.0(3)
C(1)—C(2)—C(3)	120.7(3)	C(15)—C(14)—C(13)	120.5(3)	O(1A)—C(7A)—C(2A)	122.5(3)
C(1)—C(2)—C(7)	118.9(3)	C(15)—C(14)—Cl(1)	119.5(2)	N(6A)—C(7A)—C(2A)	115.5(3)
C(3)—C(2)—C(7)	120.4(3)	C(13)—C(14)—Cl(1)	120.0(2)	C(12A)—C(8A)—C(9A)	118.0(3)
N(4)—C(3)—C(1A)	120.5(3)	C(14)—C(15)—C(9)	121.0(3)	C(12A)—C(8A)—N(6A)	122.9(3)
N(4)—C(3)—C(2)	120.5(3)	C(22)—C(21)—C(26)	119.0(3)	C(9A)—C(8A)—N(6A)	119.1(3)
C(1A)—C(3)—C(2)	119.0(3)	C(22)—C(21)—C(10)	120.6(3)	C(15A)—C(9A)—C(8A)	119.1(3)
C(5)—N(4)—C(3)	119.3(2)	C(26)—C(21)—C(10)	120.2(3)	C(15A)—C(9A)—C(10A)	120.1(3)
N(4)—C(5)—N(6)	125.5(3)	C(23)—C(22)—C(21)	120.5(3)	C(8A)—C(9A)—C(10A)	120.8(3)
N(4)—C(5)—C(11)	116.6(3)	C(24)—C(23)—C(22)	119.9(3)	C(11A)—C(10A)—C(9A)	117.4(3)
N(6)—C(5)—C(11)	117.8(3)	C(25)—C(24)—C(23)	120.3(3)	C(11A)—C(10A)—C(21A)	118.6(3)
C(7)—N(6)—C(5)	118.1(2)	C(24)—C(25)—C(26)	119.9(3)	C(9A)—C(10A)—C(21A)	124.0(3)
C(7)—N(6)—C(8)	122.0(2)	C(25)—C(26)—C(21)	120.4(3)	C(10A)—C(11A)—C(5A)	125.0(3)
C(5)—N(6)—C(8)	119.8(2)	C(3)—C(1A)—C(2A)	120.3(3)	C(13A)—C(12A)—C(8A)	121.6(3)
O(1)—C(7)—N(6)	122.8(3)	C(1A)—C(2A)—C(3A)	119.7(3)	C(14A)—C(13A)—C(12A)	119.5(3)
O(1)—C(7)—C(2)	121.3(3)	C(1A)—C(2A)—C(7A)	120.0(3)	C(13A)—C(14A)—C(15A)	121.2(3)
N(6)—C(7)—C(2)	115.9(3)	C(3A)—C(2A)—C(7A)	120.3(3)	C(13A)—C(14A)—Cl(1A)	119.6(2)
C(12)—C(8)—C(9)	118.0(3)	N(4A)—C(3A)—C(1)	119.1(3)	C(15A)—C(14A)—Cl(1A)	119.2(2)
C(12)—C(8)—N(6)	122.2(3)	N(4A)—C(3A)—C(2A)	121.0(3)	C(14A)—C(15A)—C(9A)	120.6(3)
C(9)—C(8)—N(6)	119.8(3)	C(1)—C(3A)—C(2A)	119.9(3)	C(26A)—C(21A)—C(22A)	119.3(3)
C(15)—C(9)—C(8)	119.5(3)	C(5A)—N(4A)—C(3A)	119.2(3)	C(26A)—C(21A)—C(10A)	118.4(3)
C(15)—C(9)—C(10)	120.8(3)	N(4A)—C(5A)—N(6A)	125.9(3)	C(22A)—C(21A)—C(10A)	122.2(3)
C(8)—C(9)—C(10)	119.7(3)	N(4A)—C(5A)—C(11A)	115.9(3)	C(23A)—C(22A)—C(21A)	119.9(3)
C(11)—C(10)—C(9)	119.0(3)	N(6A)—C(5A)—C(11A)	118.1(3)	C(24A)—C(23A)—C(22A)	120.1(3)
C(11)—C(10)—C(21)	119.7(3)	C(5A)—N(6A)—C(8A)	119.5(2)	C(25A)—C(24A)—C(23A)	120.2(3)
C(9)—C(10)—C(21)	121.3(3)	C(5A)—N(6A)—C(7A)	118.1(2)	C(24A)—C(25A)—C(26A)	120.2(3)
C(10)—C(11)—C(5)	123.7(3)	C(8A)—N(6A)—C(7A)	122.4(2)	C(25A)—C(26A)—C(21A)	120.2(3)
C(13)—C(12)—C(8)	121.3(3)				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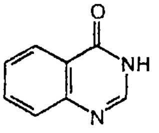
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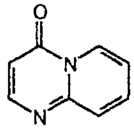
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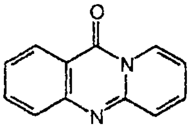
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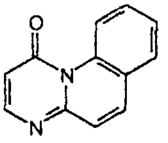
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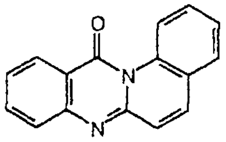
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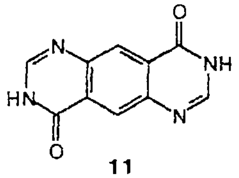
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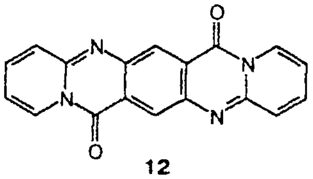
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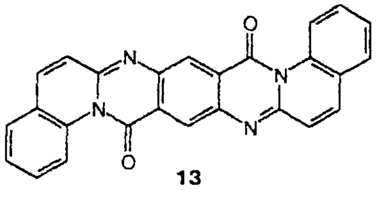
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and Cl(1A)...C(22)' (1−*x*, 2−*y*, 1−*z*) [3.29 Å] intermolecular contacts are also found in the crystal.

The distinction in the conformations of the dihydropyrimidinone cycles in structure **1** is of particular interest. In accordance with theoretical[11] and experimental[12—14] data, the equilibrium conformation of the partly hydrogenated ring in 6-oxo-1,6-dihydropyrimidine is planar. However, it has been shown previously[11,15] that this dihydrocycle exhibits a rather high conformational flexibility and its conversion to the conformation of a distorted sofa with the =C—N—C(=O)—C= torsion angle of ±20° requires merely 1.4 kcal mol^{-1}. In this connection it remains unclear whether the observed deformation of the pyrimidinone cycle in **1** is due to intramolecular factors or it is a result of intermolecular interactions in the crystal. To resolve this issue, we calculated the equilibrium geometry and studied the conformational flexibility of model compounds **5**—**13**.

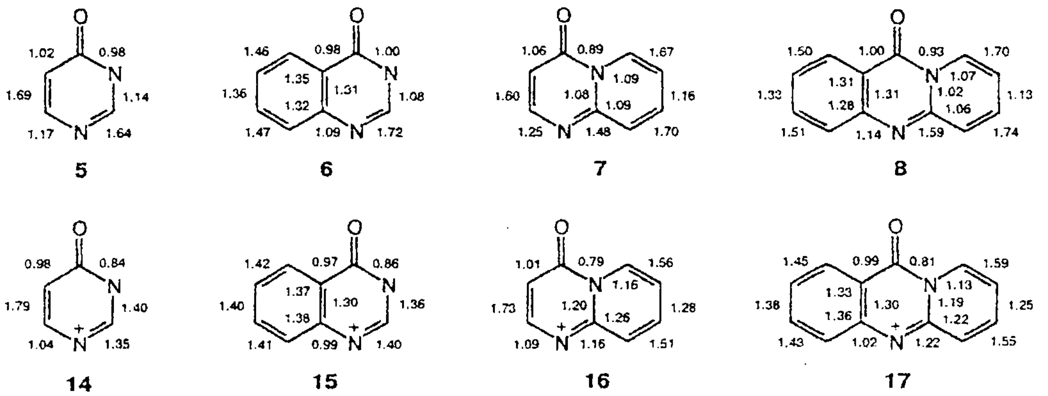
Previously,[11,16,17] it has been shown that the equilibrium conformation of 6-oxo-1,6-dihydropyrimidine is defined by two factors. The first factor is the conjugation between the lone electron pair of the bridged nitrogen atom and the double bonds of the cycle and the C=O group, which is maximum if the cycle is planar. However, in this case a 7-π-electron cyclic conjugated system of non-aromatic character is formed, which destabilizes the planar conformation. According to the data of calculations, the equilibrium conformation of the cycle in compounds **5**—**8**, **11**, and **12** is planar, which indicates the predominance of flattening factors. The unfavorable nonvalence interactions between the oxygen atom of the carbonyl group and the carbon atom in the *peri*-position of the aromatic ring in molecules **9**, **10**, and **13** result in conversion of the dihydrocycle to a conformation close to a half-chair conformation. The data of calculations show that unlike **1**, the equilibrium conformation of both dihydrocycles in **13** is equally nonplanar (the =C—N—C(=O)—C= torsion angles in two dihydrocycles are equal to 13.7° and −13.7°, respectively). Thus, the conformational nonequivalence of the dihydropyrimidinone cycle observed in the crystal is most likely due to the packing effects.

The analysis of the crystal structure of **1** showed that it has a stacking character. The molecules in the stack are parallel to one another, and the distance between them is ~4 Å. Because of this, the nonvalence interactions of the basic molecule with two adjacent molecules in the stack can result in flattening the partly hydrogenated rings in the crystal.

The effect of two factors acting in opposite directions and defining the conformation of the dihydrocycle results in a high conformational flexibility of the partly hydrogenated ring in structures **5**—**13**, analogous to that in monocyclic compounds **8** and **12**. The conversion of the dihydropyrimidine cycle from the planar equilibrium conformation to a distorted sofa conformation with the =C—N—C(=O)—C= torsion angle of ±20° leads to a less than 2 kcal mol^{-1} increase in the energy of the molecules (see Table 8). A study of the conformational dynamics of compounds **5**—**13** shows that the annelation of the dihydrocycle either at the C=C (**6**) or at the C—N (**7**) bond has almost no effect on its flexibility. In the case of dibenzo annelated derivative **8**, an appreciable increase in the flexibility of the dihydrocycle is observed. This fact is most likely associated with the weakening of the conjugation between the carbonyl group and the aromatic rings, which is characteristic, in particular, of antraquinone.[18] This assumption is also confirmed by the decrease in the sum of the orders of the endocyclic bonds with participation of the carbonyl carbon atom and by localization of charges on the C=O group in the series of compounds **5**—**8** (Schemes 1 and 2). In the case of compounds **9** and **10**, a further increase in the flexibility of the dihydrocycle is observed because of unfavorable nonvalence interactions between the oxygen atom of the carbonyl group and the carbon atom in the *peri*-position of the aromatic ring, which are maximum for a planar conformation. An analogous tendency for the flexibility of the dihydrocycle to increase is also retained in the series of compounds **11**—**13** having two 6-oxo-1,6-dihydropyrimidine cycle. It should also be noted that the change in the energy of molecules **11**—**13** in the case of a simultaneous symmetric and antisymmetric change of two =C—N—C(=O)—C= torsion angles is nearly equal.

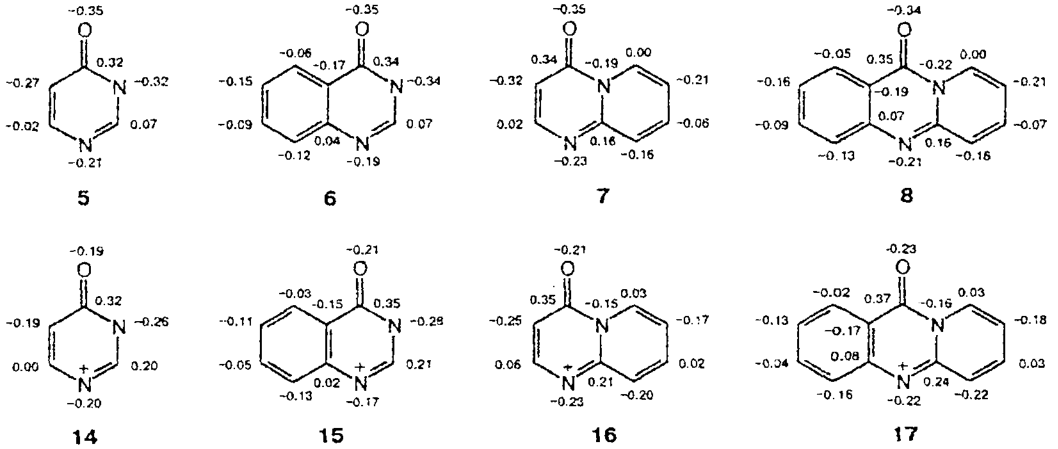
Scheme 1

Bond orders in compounds 5—8 and 14—17



Scheme 2

Charges on the atoms in compounds 5—8 and 14—17



The presence of two pyridine nitrogen atoms in compound **1** is responsible for the fairly easy protonation of **1** in acidic medium. However, unlike pyridine and pyrimidine, this leads to an essential change in the molecular geometry (compound **2**, Fig. 2, Tables 4—6). In the crystal, molecule **2** is in a special position at the center of symmetry coinciding with the center of the C(1)...C(3), C(1A)...C(3A) ring. Unlike **1**, the dihydropyrimidinone cycle has a sofa conformation. The N(6) atom deviates from the plane of the rest of atoms of the ring by 0.16 Å. The dihydropyridine ring has a twist-boat conformation. The C(5) and N(6) atoms deviate from the plane of the remaining atoms of the ring by —0.13 and —0.21 Å, respectively. Because of the nonplanar geometry of dihydrocycles, molecule **2** is severely bent. The dihedral angle between the planes of the C(1)...C(3),

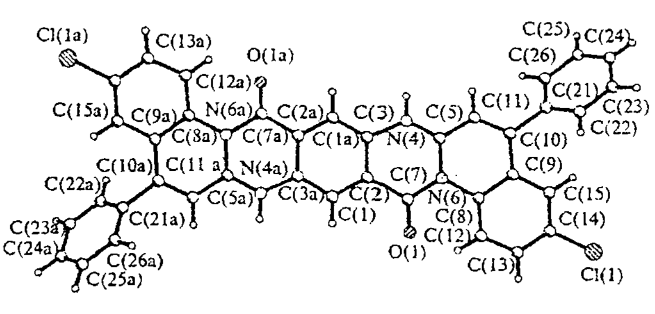


Fig. 2. The structure of cation of compound **2**.

Table 4. Coordinates (×10^4) and equivalent isotropic thermal parameters (U_{eq}×10^3) of nonhydrogen atoms in structure **2**

Atom	x	y	z	U_{eq}/Å^2
Cl(1)	9030(1)	−14(1)	2112(3)	40(1)
O(1)	7392(2)	−1347(2)	−3708(7)	45(2)
C(1)	7048(3)	−2154(2)	−5339(10)	33(2)
C(2)	7612(3)	−2094(2)	−4205(10)	27(2)
C(3)	8078(3)	−2439(2)	−3920(9)	26(2)
N(4)	8657(3)	−2340(2)	−2831(8)	34(2)
C(5)	8802(3)	−1958(2)	−2062(9)	26(2)
N(6)	8337(3)	−1622(2)	−2135(7)	25(2)
C(7)	7743(3)	−1653(2)	−3393(10)	28(2)
C(8)	8489(4)	−1221(3)	−1169(10)	35(2)
C(9)	9147(3)	−1153(2)	−430(8)	22(2)
C(10)	9620(3)	−1491(2)	−486(9)	24(2)
C(11)	9429(3)	−1885(2)	−1183(9)	25(2)
C(12)	8023(4)	−922(2)	−875(9)	30(2)
C(13)	8203(4)	−549(2)	110(9)	29(2)
C(14)	8827(3)	−473(2)	799(9)	24(2)
C(15)	9309(3)	−768(2)	585(9)	23(2)
C(21)	10333(3)	−1427(2)	250(10)	34(2)
C(22)	10660(3)	−1050(2)	−168(10)	31(2)
C(23)	11305(3)	−1001(3)	544(10)	33(2)
C(24)	11625(3)	−1336(3)	1549(10)	33(2)
C(25)	11311(4)	−1701(3)	1928(10)	44(2)
C(26)	10660(3)	−1764(2)	1235(9)	28(2)
F(1S)	5829(3)	−1553(2)	−1379(10)	114(2)
F(2S)	5999(3)	−2055(3)	−3083(8)	109(2)
F(3S)	5651(2)	−2227(2)	−915(9)	89(2)
O(1S)	6937(3)	−2432(2)	−591(9)	79(2)
O(2S)	7039(4)	−1718(3)	103(13)	118(2)
C(1S)	6763(5)	−2033(3)	−575(12)	58(2)
C(2S)	6060(5)	−1970(4)	−1441(14)	64(2)
F(4S)	5856(5)	−1470(3)	2796(18)	93(2)
F(5S)	5131(13)	−1209(8)	4303(27)	185(3)
F(6S)	5008(6)	−1187(4)	1537(17)	107(3)
O(3S)	5264(5)	−2227(4)	2978(14)	50(2)
O(4S)	4299(4)	−1900(3)	2443(13)	38(2)
C(3S)	4885(10)	−1879(4)	2637(31)	55(3)
C(4S)	5209(7)	−1421(6)	2810(25)	57(3)
O(5S)	1991(8)	4694(6)	6097(27)	138(3)
O(6S)	2233(7)	4542(4)	3606(19)	74(3)
C(5S)	1889(14)	4538(6)	4455(30)	107(3)
O(1W)	821(16)	4483(7)	−2062(32)	300(3)
O(2W)	1692(7)	4206(5)	948(25)	127(3)

Table 5. Bond lengths (*d*) in structure **2**

Bond	*d*/Å	Bond	*d*/Å
Cl(1)—C(14)	1.739(7)	O(1)—C(7)	1.179(8)
C(1)—C(2)	1.37(1)	C(1)—C(3A)	1.36(1)
C(2)—C(3)	1.416(9)	C(2)—C(7)	1.48(1)
C(3)—N(4)	1.399(8)	C(3)—C(1A)	1.36(1)
N(4)—C(5)	1.311(9)	C(5)—N(6)	1.400(9)
C(5)—C(11)	1.400(9)	N(6)—C(7)	1.462(9)
N(6)—C(8)	1.437(9)	C(8)—C(9)	1.423(9)
C(8)—C(12)	1.38(1)	C(9)—C(10)	1.43(1)
C(9)—C(15)	1.42(1)	C(10)—C(11)	1.339(9)
C(10)—C(21)	1.53(1)	C(12)—C(13)	1.38(1)
C(13)—C(14)	1.35(1)	C(14)—C(15)	1.38(1)
C(21)—C(22)	1.40(1)	C(21)—C(26)	1.39(1)
C(22)—C(23)	1.387(9)	C(23)—C(24)	1.38(1)
C(24)—C(25)	1.34(1)	C(25)—C(26)	1.40(1)
F(1S)—C(2S)	1.35(1)	F(2S)—C(2S)	1.32(1)
F(3S)—C(2S)	1.28(1)	O(1S)—C(1S)	1.25(1)
O(2S)—C(1S)	1.19(1)	C(1S)—C(2S)	1.53(1)
F(4S)—C(4S)	1.37(2)	F(6S)—C(4S)	1.25(2)
F(5S)—C(4S)	1.39(3)	O(3S)—C(3S)	1.32(2)
C(3S)—C(4S)	1.53(2)	O(4S)—C(3S)	1.22(2)
O(5S)—C(5S)	1.37(3)	O(6S)—C(5S)	1.08(3)

Table 6. Bond angles (ω) in structure **2**

Angle	ω/deg	Angle	ω/deg	Angle	ω/deg
C(2)—C(1)—C(3A)	118.9(6)	C(1)—C(2)—C(3)	120.4(6)	C(21)—C(26)—C(25)	118.5(7)
C(1)—C(2)—C(7)	118.6(6)	C(3)—C(2)—C(7)	120.9(6)	O(1S)—C(1S)—C(2S)	111.9(8)
C(2)—C(3)—N(4)	116.7(6)	C(2)—C(3)—C(1A)	120.6(6)	F(1S)—C(2S)—F(2S)	104.1(9)
N(4)—C(3)—C(1A)	122.7(6)	C(3)—N(4)—C(5)	125.5(6)	F(2S)—C(2S)—F(3S)	104.9(8)
N(4)—C(5)—N(6)	120.5(6)	N(4)—C(5)—C(11)	119.4(6)	F(2S)—C(2S)—C(1S)	109.8(9)
N(6)—C(5)—C(11)	120.1(6)	C(5)—N(6)—C(7)	119.5(5)	O(3S)—C(3S)—O(4S)	123.2(13)
C(5)—N(6)—C(8)	119.6(5)	C(7)—N(6)—C(8)	120.2(5)	O(4S)—C(3S)—C(4S)	118.9(13)
O(1)—C(7)—C(2)	122.9(6)	O(1)—C(7)—N(6)	121.8(6)	F(4S)—C(4S)—F(6S)	104.3(16)
C(2)—C(7)—N(6)	115.3(5)	N(6)—C(8)—C(9)	116.8(6)	F(4S)—C(4S)—C(3S)	109.3(15)
N(6)—C(8)—C(12)	122.6(6)	C(9)—C(8)—C(12)	120.5(7)	F(6S)—C(4S)—C(3S)	110.6(15)
C(8)—C(9)—C(10)	121.3(6)	C(8)—C(9)—C(15)	118.1(6)	O(1S)—C(1S)—O(2S)	130.1(9)
C(10)—C(9)—C(15)	120.0(5)	C(9)—C(10)—C(11)	118.7(6)	O(2S)—C(1S)—C(2S)	117.6(9)
C(9)—C(10)—C(21)	122.8(6)	C(11)—C(10)—C(21)	118.4(6)	F(1S)—C(2S)—F(3S)	106.2(9)
C(5)—C(11)—C(10)	122.2(6)	C(8)—C(12)—C(13)	119.4(7)	F(1S)—C(2S)—C(1S)	115.1(8)
C(12)—C(13)—C(14)	121.1(7)	Cl(1)—C(14)—C(13)	119.8(5)	F(3S)—C(2S)—C(1S)	115.6(9)
Cl(1)—C(14)—C(15)	118.4(5)	C(13)—C(14)—C(15)	121.7(6)	O(3S)—C(3S)—C(4S)	116.9(15)
C(9)—C(15)—C(14)	119.1(6)	C(10)—C(21)—C(22)	120.4(6)	F(4S)—C(4S)—F(5S)	109.1(16)
C(10)—C(21)—C(26)	118.7(6)	C(22)—C(21)—C(26)	120.7(6)	F(5S)—C(4S)—F(6S)	111.5(18)
C(21)—C(22)—C(23)	118.6(7)	C(22)—C(23)—C(24)	120.2(7)	F(5S)—C(4S)—C(3S)	111.7(19)
C(23)—C(24)—C(25)	120.8(7)	C(24)—C(25)—C(26)	120.8(7)	O(5S)—C(5S)—O(6S)	126.2(24)

C(1A)...C(3A) and C(8), C(9), C(12)...C(15) benzene rings is equal to 19.5°, whereas the same angles are equal to 3.5° and 1.6° for the two parts of molecule **1**. The shortening of the C(5)—N(6) bond to 1.400(9) Å and the decrease in the endocyclic N(4)—C(5)—N(6) bond angle to 120.5° as compared to those in compound **1** (1.425(4) Å and 125.5(3)°, respectively) are also observed in molecule **2**. Most likely, this can be explained by the contribution of the 1,4-dihydrotautomeric form to the structure of the protonated dihydrocycle.

As in compound **1**, the phenyl substituent is rotated with respect to the endocyclic C(10)—C(11) double bond (the C(11)—C(10)—C(21)—C(22) torsion angle is equal to −44(1)°).

As in compound **1**, there are shortened H(12A)...O(1) [2.14 Å] (the sum of the van der Vaals radii[7] is equal to 2.45 Å) intramolecular contacts in compound **2**, which destabilize the planar conformation due to the O(1)...C(12) [2.73 Å] (3.00 Å) interactions of repulsive character.

Protonation of **1** with the formation of compound **2** and the intermolecular H(4A)...O(4S)′ (0.5+*x*, −1.5−*y*, −0.5+*z*) (the H...O distance is equal to 1.78 Å, the N—H...O angle is equal to 159.7°) hydrogen bonds occurs through a molecule of trifluoroacetic acid. Molecules **2** are stacked in the crystal. The distance between the central benzene rings of two adjacent molecules in the stack is ~7 Å. However, they have a different structure as compared with that in **1**. The stacks in the crystal of **2** are arranged in such a way that channels are formed between them; the molecules of the solvent are located in these channels to form the shortened H(1A)...F(4S)′ (*x*, *y*, 1−*z*) [2.47 Å] (the sum of the van der Vaals radii is equal to 2.56 Å) intermolecular contacts. It should also be noted that the phenyl substituents of each molecule from two adjacent stacks are "wedged" between two molecules of the adjacent stack. This results in approaching molecules **2** in the crystal and the formation of the shortened H(1A)...C(3)′ (1.5−*x*, −0.5−*y*, −1−*z*) [2.03 Å] (the sum of the van der Vaals radii[7] is equal to 2.87 Å), H(4A)...C(1)′ (1.5−*x*, −0.5−*y*, −1−*z*) [2.57 Å] (2.87 Å), Cl(1)...H(22A)′ (2−*x*, −*y*, −*z*) [2.99 Å] (3.06 Å), and Cl(1)...C(14)′ (2−*x*, −*y*, −*z*) [3.38 Å] (3.61 Å) intermolecular contacts.

Calculations of the structure of protonated analogs of compounds **5**—**13** (structures **14**—**22**) showed that the equilibrium conformation of molecules **14**—**17**, **20**, and **21** is planar, which is in agreement with experimental data for the 1-methyl-6-oxo-1,6-dihydropyrimidine cation.[19] As in molecules **9**, **10**, and **13**, the dihydropyrimidone ring in compounds **18**, **19**, and **22** has a half-chair conformation; however, the degree of puckering of the dihydrocycle in protonated derivatives is somewhat higher (see Table 7).

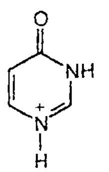
Investigation of the conformational flexibility of cations **14**—**22** gives a clearer picture of the increase in the flexibility of the dihydrocycle in the case of its annelation in the series of compounds **14**—**19**, and **20** and **21** (see Table 8). As in the case of unprotonated analogs **11**—**13**, the change in the energy of molecules **20**—**22** for both symmetric and antisymmetric scanning the two =C—N—C(=O)—C= torsion angles is nearly the same. A comparison between the conformational dynamics of compounds **5**—**13** and that of the corresponding cations indicates a tendency for the flexibility of the 6-oxo-1,6-dihydropyrimidine cycle to increase upon protonation.

Table 7. Torsion angles and puckering parameters of the dihydrocycle in compounds **9**, **10**, **13**, **18**, **19**, and **22** *

Compound	Torsion angle/deg**		Puckering parameters		
	α_1	α_2	S	θ	ψ
9	9.1	2.8	0.12	52.0	17.8
10	12.6	4.4	0.16	54.4	19.7
13	13.7	4.7	0.17	54.3	21.2
18	13.7	4.0	0.17	51.0	25.2
19	17.0	5.5	0.21	53.3	28.0
22	16.3	5.1	0.20	52.8	27.2

* The rest of the molecules have a planar equilibrium conformation.

** α_1 = =C—N—C(=O)—C=, α_2 = C=C—N=C.



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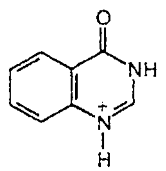

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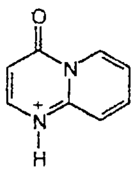

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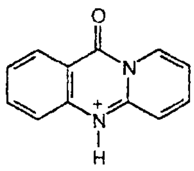

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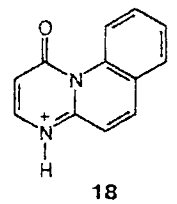

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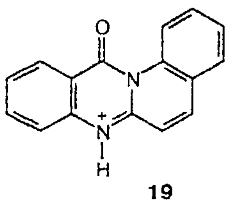

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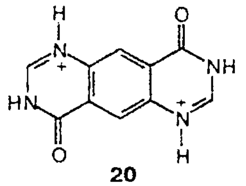

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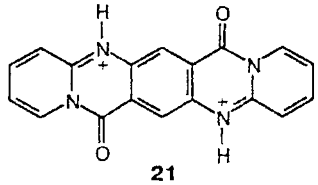

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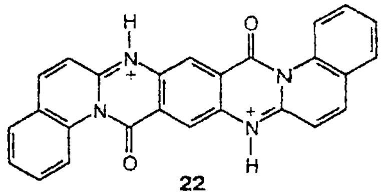

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Table 8. The energy change (kcal mol^{-1}) at different torsion angles in compounds **5—22**

Compound	Torsion angle =C—NH—C(=O)—C=/deg			
	0	10	20	30
5	0	0.5	2.0	3.9
6	0	0.4	1.7	3.9
7	0	0.4	1.7	4.0
8	0	0.3	1.4	3.3
9	0.1	0.01	0.5	1.9
10	0.4	0.03	0.2	1.2
11*	0	0.8	3.2	7.5
11**	0	0.8	3.2	7.5
12*	0	0.6	2.6	6.0
12**	0	0.6	2.6	6.0
13*	0.8	0.1	0.3	2.1
13**	0.8	0.1	0.3	2.0
14	0	0.5	1.9	4.3
15	0	0.4	1.7	3.9
16	0	0.3	1.3	3.1
17	0	0.3	1.1	2.7
18	0.4	0.04	0.1	1.0
19	0.7	0.1	0.03	0.7
20*	0	0.8	3.4	7.8
20**	0	0.8	3.4	7.8
21*	0	0.5	2.2	5.3
21**	0	0.5	2.2	5.2
22*	1.1	0.2	0.1	1.4
22**	1.1	0.2	0.1	1.4

* Symmetric change of torsion angles. ** Antisymmetric change of torsion angles.

This is most likely associated with the appreciable contribution of the 1,4-dihydrotautomeric form to the structure of the protonated cycle, resulting in a decrease in the conjugation between the carbonyl group and the lone electron pair of the adjacent nitrogen atom. This assumption is confirmed by a pronounced equalization of the lengths and orders of the $C=N^+$ and C(=O)—N bonds (see Scheme 1).

Thus, in fused systems, the 1,6-dihydropyrimidine cycle exhibits a high conformational flexibility and can have a nonplanar equilibrium conformation. Protonation of such molecules results in a further folding of the dihydrocycle and in a decrease in its rigidity. These peculiarities of the structure and dynamics of the molecules considered can have a pronounced effect on physicochemical properties of the polymers containing fused heterocycles in the main chain. The main quantitative characteristic of these rigid-chain polymers is the length of the Kuhn segment. This quantity makes it possible to estimate the ability of a macromolecule to form (depending on its geometric structure) a coil, and a bent or rigid straight rod. To prove the above assumption, we calculated the lengths of the Kuhn segment (A_{fr}) under the assumption of free rotation about virtual bonds by the Monte-Carlo method using the procedure described in Ref. 21. The geometric structure of the repeating unit of the polymer (the lengths of virtual bonds and the angles between them, Fig. 3) was constructed on the basis of quantum-chemical calculations of model compounds **1** and **2**. The calculated A_{fr} value for the planar conformation of the repeating unit appeared to be equal to ∞, *i.e.*, in this case the polymer is a rigid rod.

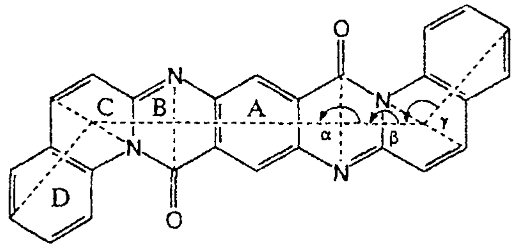

Fig. 3. Model representation of the monomer repeating unit on the basis of compound **1**: α is the angle between the A and B planes; β is the angle between the B and C planes; and γ is the angle between the C and D planes.

Due to the high conformational flexibility of dihydropyrimidine cycles (see Table 7), the polymer can contain repeating units with different degrees of puckering of partly hydrogenated rings. In this case, the repeating unit of the macromolecule can have a distorted boat or a distorted chair shape (*cis*- and *trans*-conformation, respectively) depending on the signs of two =C—N—C(=O)—C= torsion angles. To estimate the effect of the presence of nonplanar cycles in the chain on the rigidity of the polymer, we considered a polymer consisted only of the repeating units in *cis*- or *trans*-conformation, which had a fixed =C—N—C(=O)—C= torsion angle. As can be seen in Table 9, in the case of *trans*-conformations A_{fr} has an infinite value ($A_{\text{fr}} = \infty$) at any torsion angle. For *cis*-conformations, A_{fr} has a finite value already at a torsion angle of 10°. As can also be seen in Table 9, polymers based on the protonated form of **1** are more sensitive to changes in the conformation of dihydrocycles.

In a real polymer, dihydropyrimidinone rings with different values of torsion angles are present. Thus, the polymer can be considered as a copolymer consisting of repeating units with a continuous spectrum of the torsion angle values. To simulate a real macromolecule, we considered a polymer consisting of seven types of repeating units (see Table 9). Having assumed an equiprobable entrance of the repeating units of each type into the polymeric chain, one can calculate the length of the Kuhn segment of the copolymer using the known procedure.[22] The A_{fr} values are equal to 1632 Å and 1403 Å in the case of copolymers with unprotonated and protonated monomers, respectively.

Thus, the results obtained confirm the substantial effect of conformational flexibility of the dihydropyrimidinone cycle in 7,9a,16,18a-tetrazadi-

Table 9. Geometric characteristics of the repeating units (see Fig. 3) and the lengths of the Kuhn segment of the polymers based on compounds **1** and **2**

Confor-mation	Torsion angle C=N—C(=O)—C=/deg	The contour length* l_0/Å	α	β	γ	Length of the Kuhn segment/Å
				deg		
			Compound **1**			
trans	±13.6**	18.655	172.9	173.0	172.5	1083
cis	10	18.679	174.3	177.5	178.4	2566
trans	10	18.669	175.0	174.2	172.7	∞
cis	20	18.638	169.4	171.2	172.7	731
trans	20	18.637	169.3	171.2	172.8	∞
cis	30	18.616	163.9	168.4	174.0	533
trans	30	18.612	163.7	168.1	173.9	∞
			Compound **2**			
trans	±17.0**	18.729	171.5	173.0	173.4	947
cis	10	18.740	175.3	174.4	173.4	1890
trans	10	18.734	175.1	174.5	173.5	∞
cis	20	18.720	169.1	172.3	173.8	547
trans	20	18.723	168.6	172.5	173.9	∞
cis	30	18.701	163.0	170.0	175.0	408
trans	30	18.697	162.5	170.2	174.9	∞

* The length of a broken line connecting the centers of virtual bonds for rigid-chain polymers.

** The value of the torsion angle corresponding to the equilibrium conformation.

benzo[*a*,*l*]pentacene-9,18-dione on the length of the Kuhn segment in rigid-chain heterocyclic polymers built on the basis of such repeating units.

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