atoms. The weighting scheme for the reflections in the LSM, *f*-curves employed, and the anomalous-dispersion corrections to them ($\Delta f'$ and $\Delta f''$) are indicated elsewhere.[10] All the X-ray calculations were performed on a PDP11/23 mini-computer using a SDP-PLUS program system designed by «Enraf-Nonius».

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Synthesis, structure, and physico-chemical properties of 3-methyl and 3,3-dimethyl derivatives of 1-(4',4'-dimethyl-2',6'-dioxocyclohex-1'-yl)-3,4-dihydroisoquinoline

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3,3-Dimethyl- and 3-methyl-1-(4',4'-dimethyl-2',6'-dioxocyclohex-1'-yl)-3,4-dihydroisoquinolines have been synthesized. Crystal and molecular structures of the 3,3-dimethyl derivative have been determined. In the crystalline state this compound exists as a tautomeric form where a hydrogen atom is located at the N atom of the dihydroisoquinoline fragment of the molecule. The tautomeric equilibrium does not shift noticeably in solutions, as shown by IR, UV, and NMR spectroscopy.

Key words: isoquinoline derivatives; dimedone derivatives; structure, X-ray study; tautomerism, spectroscopic study.

It is known that isoquinoline (benzo[*c*]pyridine) and dimedone (5,5-dimethyl-1,3-cyclohexanedione) derivatives are pharmacologically active.[1,2] In a search for new biologically active compounds of higher practical value we have set ourselves the task of synthesizing isoquinoline derivatives containing a dimedone moiety as a substituent. The structure of such compounds is of interest by itself and merits detailed consideration, since both dimedone and 3,4-dihydroisoquinoline derivatives are capable of tautomeric transformations. In particular, dimedone (**1**), possessing acidic properties (pK_a 5.2), can exist in the keto (***k***) as well as in the enol (***e***) tautomeric form. The equilibrium between them is determined by the aggregative state of the compound as well as by the

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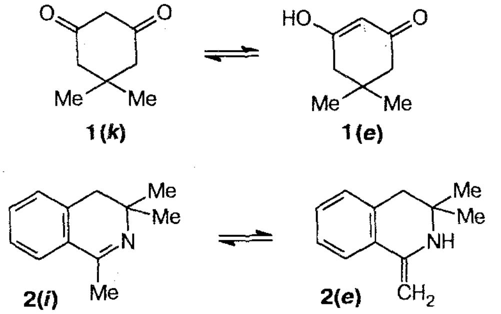
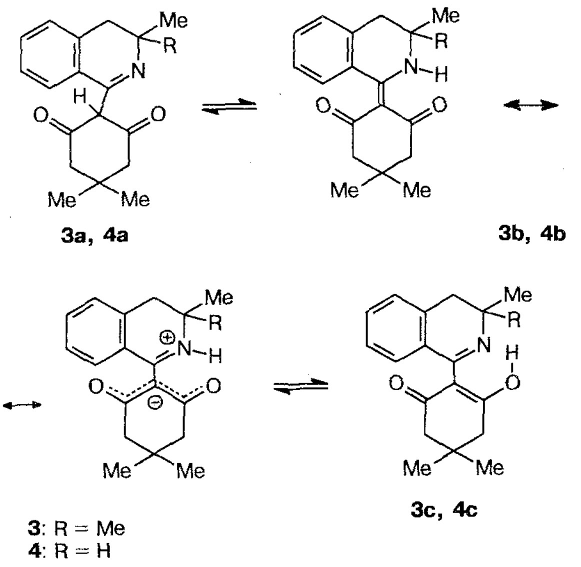
type and size of the substituent in position 2 (see ref.[3]). By contrast, isoquinolines display basic properties (the pK_a of isoquinoline is 5.40).[4] An isoquinoline derivative such as 1,3,3-trimethyl-3,4-dihydroisoquinoline (**2**) may be able to exist not only in the imine (*i*) form but also as the enamine (*e*). This possibility can be inferred from some peculiarities of its chemical properties and from the temperature-dependent broadening of its signals in the ^{1}H NMR spectrum.[5]



1(*k*) **1**(*e*)

2(*i*) **2**(*e*)

Taking into account the acid-base properties and tautomerism of both dimedone and isoquinoline derivatives, one can represent the structure of 3,3-dimethyl and 3-methyl derivatives of 1-(4',4'-dimethyl-2',6'-dioxocyclohex-1'-yl)-3,4-dihydroisoquinoline (compounds **3** and **4**, respectively) by the following structures:



3a, 4a **3b, 4b**

3c, 4c

3: R = Me
4: R = H

The purpose of the present work has been the synthesis and investigation of the structural and physico-chemical characteristics of compounds **3** and **4**.

Experimental

3,3-Dimethyl-1-(4',4'-dimethyl-2',6'-dioxocyclohex-1'-yl)-3,4-dihydroisoquinoline (3). A mixture of 1-methylthio-3,3-dimethyl-3,4-dihydroisoquinoline prepared according to ref.[6] (10.25 g, 0.05 mol) with 5,5-dimethylcyclohexane-1,3-dione (9.0 g, 0.05 mol) was refluxed in 100 mL of acetic acid for ~2 h until the spot of the isoquinoline on the TLC plate dissapeared (Silufol UV 254, chloroform—acetone mixture, 9:1 v/v, as eluent; 0.5 % solution of chloranil in benzene as spraying reagent). The reaction mixture was poured into 200 mL of water and neutralized by aqueous ammonia. On cooling a precipitate was isolated which was then recrystallized from hexane—isopropanol mixture (4:1). The yield of **3** was 2.9 g (80 %), m p 178.5—180°C. Single crystals used in the X-ray structural analysis were obtained by recrystallization of **3** from acetone.

Compound **4** was synthesized by a similar procedure.

The X-ray study of compound **3** was carried out using a Sintex-P 21 four-circle automatic diffractometer (θ/2θ scan mode, Mo K_α radiation, graphite monochromator, $2\theta_{max}$ = 50°, 1639 independent reflections with $I \geq 3\sigma$, without regard for the sample absorption). Found: a = 10.435(3) Å, b = 13.644(2) Å, c = 2.82(3) Å, β = 91.89(2)°; V = 1630.8(8) Å^3. Space group $P\,2_1$; d_{calc} = 1.13 g cm^{-3}, Z = 4. The structure was solved by the direct method using SHELX programs and refined by the least squares method in the full-matrix isotropic approximation and then in the anisotropic approximation. All hydrogen atoms were identified from the electron-density difference maps. The final R value was 0.037. Coordinates of independent atoms are given in Table 1, numbering of the atoms in the molecules is shown in Fig.1.

The IR spectra were recorded on a Specord 75-IR spectrophotometer. Solvents (CCl$_4$, CH$_3$CN, dioxane) were purified by standard procedures.[7] Integral intensities of absorption bands were calculated according to ref.[8]:

$$A = k/(cl)\,\ln(T_0/T_{\nu_{max}})\Delta\nu^a_{1/2}.$$

The electron absorption spectra were obtained with a Specord UV VIS and a Specord M-40 spectrophotometers.

^{1}H and ^{13}C NMR spectra of compound **1** were measured on a Bruker WP-200 SY spectrometer in C$_6$D$_6$ and in CDCl$_3$, respectively. Chemical shifts are referred to TMS (^{1}H) and to carbon atoms of the solvent (^{13}C).

^{1}H NMR spectrum . δ: 0.73 (2 CH$_3$); 0.97 (2 CH$_3$); 2.19 (CH$_2$); 2.48 (2 CH$_2$); 6.83 (1 H arom.); 7.17 (2 H arom.); 7.95 (1 H arom.).

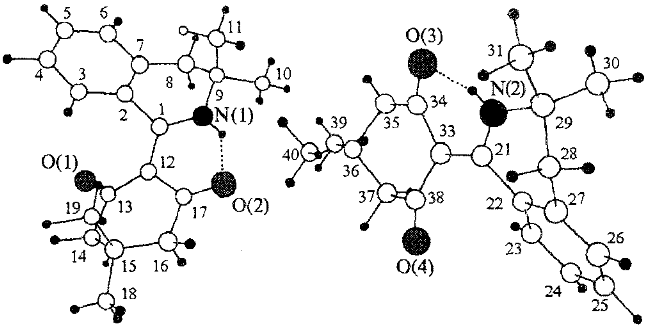


Fig. 1. 3,3-dimethyl-1-(4',4'-dimethyl-2',6'-dioxocyclohex-1'-yl)-3,4-dihydroisoquinoline (**3**) molecules. Here and on Fig. 2 the smaller numerical indices correspond to the numbering of carbon atoms.

Table 1. Atomic coordinates in fractions of unit cell edges and temperature factors, B_{iso} and B_{eq}, for 3,3-dimethyl-1-(4',4'-dimethyl-2',6'-dioxocyclohex-1'-yl)-3,4-dihydroisoquinoline (**3**)

Atom	*x*	*y*	*z*	B_{iso}/B_{eq}
O(1)	0.4219(4)	0.3564(0)	0.6787(3)	4.0
O(2)	0.1124(3)	0.5995(3)	0.6792(4)	4.2
O(3)	−0.0619(3)	0.0989(3)	0.8524(4)	4.5
O(4)	−0.3693(4)	−0.1463(3)	0.8736(3)	4.3
N(1)	0.3198(5)	0.6353(3)	0.5746(4)	2.9
N(2)	−0.2699(4)	0.1396(3)	0.9505(4)	2.8
C(1)	0.3738(4)	0.5625(4)	0.6314(4)	2.5
C(2)	0.5157(4)	0.5566(4)	0.6246(4)	3.0
C(3)	0.5922(4)	0.5171(4)	0.7129(4)	3.5
C(4)	0.7242(5)	0.5171(5)	0.7081(5)	5.0
C(5)	0.7828(5)	0.5582(5)	0.6143(6)	5.4
C(6)	0.7077(5)	0.5971(4)	0.5282(5)	4.8
C(7)	0.5743(5)	0.5997(4)	0.5325(4)	3.3
C(8)	0.4908(5)	0.6505(4)	0.4450(4)	3.9
C(9)	0.3830(5)	0.7064(4)	0.5012(4)	3.5
C(10)	0.2838(6)	0.7422(5)	0.4127(5)	5.1
C(11)	0.4326(5)	0.7922(4)	0.5733(5)	4.6
C(12)	0.2987(4)	0.5002(3)	0.7001(4)	2.3
C(13)	0.3388(5)	0.4008(4)	0.7288(4)	3.0
C(14)	0.2715(5)	0.3497(4)	0.8252(4)	3.6
C(15)	0.1263(4)	0.3647(4)	0.8193(4)	3.3
C(16)	0.1027(4)	0.4751(4)	0.8184(5)	3.7
C(17)	0.1696(4)	0.5298(4)	0.7252(4)	3.0
C(18)	0.0657(6)	0.3160(5)	0.7152(5)	5.4
C(19)	0.0674(5)	0.3210(4)	0.9251(4)	4.2
C(21)	−0.3232(4)	0.0634(4)	0.9007(4)	2.6
C(22)	−0.4655(4)	0.0568(4)	0.9005(4)	2.8
C(23)	−0.5363(5)	0.0120(4)	0.8131(4)	3.3
C(24)	−0.6696(5)	0.0156(4)	0.8101(5)	4.2
C(25)	−0.7295(5)	0.0621(5)	0.8975(6)	4.6
C(26)	−0.6623(5)	0.1086(5)	0.9825(5)	4.4
C(27)	−0.5278(4)	0.1084(4)	0.9850(4)	3.1
C(28)	−0.4503(5)	0.1659(4)	1.0699(4)	3.3
C(29)	−0.3383(5)	0.2166(3)	1.0123(4)	2.8
C(30)	−0.3845(5)	0.2960(4)	0.9292(4)	3.7
C(31)	−0.2440(5)	0.2577(4)	1.0998(5)	3.9
C(33)	−0.2429(5)	−0.0052(4)	0.8430(4)	2.6
C(34)	−0.1137(5)	0.0231(4)	0.8171(5)	3.2
C(35)	−0.0359(5)	−0.0440(5)	0.7424(6)	3.7
C(36)	−0.1132(5)	−0.1162(4)	0.6708(4)	3.2
C(37)	−0.1985(6)	−0.1711(4)	0.7516(5)	3.6
C(38)	−0.2800(6)	−0.1073(4)	0.8255(5)	3.4
C(39)	−0.0178(8)	−0.1860(6)	0.6151(7)	4.8
C(40)	−0.1936(8)	−0.0658(6)	0.5784(6)	4.9
H(N-1)	0.253(4)	0.639(3)	0.579(3)	0(1)
H(N-2)	−0.188(7)	0.144(6)	0.944(6)	9(2)
H(C-3)	0.748(5)	0.626(4)	0.466(4)	4(1)
H(C-4)	0.780(5)	0.499(4)	0.786(4)	5(1)
H(C-5)	0.883(7)	0.557(7)	0.603(7)	11(2)
H(C-6)	0.560(4)	0.494(3)	0.781(3)	1.5(9)
H(1,C-8)	0.451(4)	0.604(3)	0.387(4)	3(1)
H(2,C-8)	0.543(5)	0.695(4)	0.391(4)	5(1)
H(110)	0.263(7)	0.687(6)	0.347(6)	9(2)
H(210)	0.207(6)	0.781(5)	0.448(5)	6(2)
H(310)	0.311(5)	0.787(4)	0.358(4)	5(1)
H(111)	0.497(6)	0.769(5)	0.633(5)	7(2)
H(211)	0.479(5)	0.843(4)	0.531(4)	5(1)
H(311)	0.366(5)	0.821(4)	0.615(4)	4(1)
H(114)	0.310(5)	0.373(4)	0.901(4)	5(1)
H(214)	0.299(6)	0.270(5)	0.816(5)	6(2)
H(116)	0.139(4)	0.498(3)	0.897(4)	2(1)
H(216)	0.023(4)	0.487(3)	0.810(3)	1.8(9)
H(118)	−0.038(6)	0.321(5)	0.706(5)	6(2)
H(218)	0.101(5)	0.342(4)	0.643(4)	4(1)
H(318)	0.084(6)	0.245(5)	0.718(5)	7(2)
H(119)	0.108(5)	0.355(5)	1.001(4)	5(1)
H(219)	0.079(7)	0.253(6)	0.943(6)	9(2)
H(319)	−0.013(5)	0.329(4)	0.927(4)	4(1)
H(C-23)	−0.497(4)	−0.019(3)	0.755(3)	1.9(9)
H(C-24)	−0.722(6)	−0.024(6)	0.731(6)	9(2)
H(C-25)	−0.821(4)	0.063(4)	0.899(4)	4(1)
H(C-26)	−0.693(4)	0.127(3)	1.044(3)	2(1)
H(128)	−0.411(4)	0.124(3)	1.125(4)	3(1)
H(228)	0.502(6)	0.716(5)	0.880(5)	6(1)
H(130)	−0.435(5)	0.346(5)	0.970(4)	5(1)
H(230)	−0.451(5)	0.271(4)	0.865(5)	5(1)
H(330)	−0.310(4)	0.329(4)	0.894(4)	3(1)
H(131)	−0.230(6)	0.210(5)	1.163(5)	6(2)
H(231)	−0.286(4)	0.299(3)	1.145(3)	1.5(9)
H(331)	−0.169(7)	0.297(6)	1.064(6)	9(2)
H(135)	0.019(5)	−0.079(5)	0.807(5)	5(1)
H(235)	0.019(5)	0.002(4)	0.697(5)	4(1)
H(137)	−0.135(7)	−0.221(5)	0.816(6)	8(2)
H(237)	−0.261(7)	−0.227(6)	0.715(6)	8(2)
H(139)	0.025(6)	−0.221(5)	0.674(6)	6(2)
H(239)	0.040(5)	−0.150(4)	0.557(4)	4(1)
H(339)	−0.057(6)	−0.231(5)	0.572(6)	6(2)
H(140)	−0.148(6)	−0.030(5)	0.525(5)	5(2)
H(240)	−0.248(6)	−0.021(4)	0.607(5)	4(1)
H(340)	−0.251(7)	−0.125(7)	0.531(6)	9(2)

Table 2. Interatomic distances in 3,3-dimethyl-1-(4',4'-dimethyl-2',6'-dioxocyclohex-1'-yl)-3,4-dihydroisoquinoline (**3**) averaged over two molecules

Bond	*d* (Å)
O(1)—C(12)	2.366(6)
O(1)—C(14)	2.365(6)
O(1)—C(13)	1.227(6)
O(2)—C(16)	2.366(7)
O(2)—C(12)	2.370(5)
O(2)—C(17)	1.236(6)
O(2)—H(N-1)	1.92(5)
N(1)—C(1)	3.155(7)
N(1)—H(N-1)	0.785(5)
N(1)—C(9)	1.474(6)
C(1)—C(2)	1.488(6)
C(1)—C(12)	1.435(6)
C(2)—C(3)	1.396(7)
C(9)—C(10)	1.528(7)
C(9)—C(11)	1.520(7)
C(10)—H(110)	1.045(6)
C(10)—H(210)	1.065(6)
C(10)—H(310)	0.97(5)
C(11)—H(111)	1.005(6)
C(11)—H(211)	0.945(5)
C(11)—H(311)	1.00(6)
C(12)—C(13)	1.458(7)
C(12)—C(17)	1.446(6)
C(13)—C(14)	1.52(7)
C(14)—C(15)	1.526(7)
C(14)—H(114)	1.11(6)
C(2)—C(7)	1.397(7)
C(3)—C(4)	1.386(7)
C(3)—H(C-3)	0.93(4)
C(4)—C(5)	1.390(9)
C(4)—H(C-4)	1.145(6)
C(5)—C(6)	1.366(9)
C(5)—H(C-5)	1.005(6)
C(6)—C(7)	1.399(7)
C(6)—H(C-6)	0.89(4)
C(7)—C(8)	1.495(7)
C(8)—C(9)	1.533(7)
C(8)—C(18)	0.98(4)
C(8)—C(28)	1.055(5)
C(14)—H(214)	1.105(6)
C(15)—C(16)	1.52(8)
C(15)—C(18)	1.529(4)
C(15)—C(19)	1.525(8)
C(16)—C(17)	1.522(8)
C(16)—H(116)	1.045(5)
C(16)—H(216)	0.93(5)
C(18)—H(118)	1.015(6)
C(18)—H(218)	1.03(5)
C(18)—H(318)	0.935(7)
C(19)—H(119)	1.01(5)
C(19)—H(219)	0.935(7)
C(19)—H(319)	0.99(6)

^{13}C NMR spectrum, δ: 165.97 (C-1); 135.06 (C-2, C-7); 120.41, 126.19, 131,02, 132,69 (C-3, C-4, C-5, C-6); 50.86 (C-8); 105.46 (C-9); 26.76 (C-10, C-11); 76.51, 77.15, 77.76 (t, C-12); 196.89 (C-13, C-14); 52.40 (C-14, C-16); 40.17 (C-15); 28.62 (C-18, C-19).

Results and Discussion

Compound **3** exists in the crystal as the **3b** tautomer. The cyclohexane fragment of the molecule is in the keto form; it adopts a chair conformation flattened at the C(12) vertex in one molecule, and a boat conformation flattened at the same vertex in the other molecule. In the first molecule the C(12) and C(15) atoms of the cyclohexanedione ring deviate from the C(17)C(16)C(14)C(13) central plane by −0.279 Å and +0.688 Å, respectively, while in the other molecule these values are +0.196 Å and +0.657 Å, respectively. The intermolecular H-bond, O—H···O, which is observed in the crystals of dimedone (O—H and O···H distances are 0.87 Å and 1.74 Å, respectively; ∠ O—H···O = 177°),[9,10] is replaced by the intramolecular N—H···O bond (N—H and H···O are 0.785 Å and 1.92 Å, respectively, ∠ N—H···O is 139.8°). The greatest alterations in interatomic distances and valence angles are observed in the β-diketone part of the dimethylcyclohexanedione fragment. The C=O bond in dimedone is markedly shorter than the C—OH bond (1.246 Å and 1.326 Å, respectively). The adjacent C(1)—C(2) and C(2)—C(3) bonds of the β-diketone fragment are also of different lengths: the C(2)—C(3) bond is longer than C(1)—C(2) by almost 0.07 Å (1.418 Å and 1.351 Å, respectively). Both C=O and C—C bonds in compound **3** are nearly equalized. The O(1)—C(13) bond is shorter than the O(2)—C(17) bond by approximately 0.01 Å (average values for the two independent molecules amount to 1.227(4)±0.02 Å and 1.236(4)±0.002 Å, respectively). Just as is the case with dimedone, a slight distinction remains between the bonds C(12)—C(13) and C(12)—C(17), conjugated wits them: the former is 1.458(6)±0.001 Å, the latter is 1.445(6)±0.001 Å long. However, both of them are 0.04—0.09 Å longer than the analogous bonds in dimedone.The lengths of the other C—C bonds in the dimethylcyclohexanedione ring do not practically differ from their typical values (Table 2).

Interatomic distances and valence angles in the 3,4-dihydroisoquinoline fragments of compound **3** are similar to those found in the cation of 1-ethoxycarbonyl-3,4-dihydroisoquinoline (**5**).[11] As in **5**, the N—C(1) distance in **3** is markedly shorter than the distance between the N atom and C(9). Their average values in compound **3** are equal to 1.312(6)±0.003 Å and 1.474±0.014 Å, respectively, whereas in **5** they are 1.296 Å and 1.468 Å. The conformations of the heterocycle moieties in **3** and **5** are, however, different: the two C atoms of the CH_2 groups in **5** deviate in different directions from the plane of the other four atoms by −0.32 Å and +0.35 Å. The dimethyldihydropyridine fragment in **3** is in a distorted half-chair conformation: the N and C(2) atoms decline in one direction from the plane of the remaining four carbon atoms (which are coplanar with the atoms of the conjugated ring with an accuracy of 0.06 Å) by +0.553 Å and +1.01 Å, respectively. The benzene ring is planar, all the bonds are equal in length and similar to the corresponding bonds in compound **5**.

When considering the system of bonds in the central fragment of the molecule, which connects its cyclohexanedione and isoquinoline moieties, one should take into account three special features of the geometry of the molecule.

1. The C(1)—C(12) bond connecting the two parts of the molecule (average distance 1.435(6)±0.008 Å) is shorter than a single $C_{sp2}—C_{sp2}$ bond (1.466 Å)[12] by approximately 0.03 Å.
2. The C(12) junction has a quasi-pyramidal shape and the C(12) atom deviates from the plane of the surrounding C(1), C(17), and C(13) atoms by 0.075 Å, whereas the configuration of the C(1) and N atoms (the latter is bound with a hydrogen atom) is practically planar.
3. The angle between the planes of the O(2)C(17)C(12)C(13)O(1) atoms and of the NC(1)C(2) atoms is equal to 27° in one molecule and to 26° in the other.

On the basis of all the bond lengths in the central part of the molecule, it can be asserted that there exists a π-interaction between its two «lateral» parts. However, the second and third of the foregoing features characterizing the molecular geometry of compound **3** suggest that this interaction is weak, and so the shortening of the C(1)—C(12) bond is partly caused by the action of Coulombic forces between the protonated heterocyclic and ionized dimedone systems. This implies that the bipolar form of the tautomer **3b** also makes a certain contribution to the bond system of the molecule.

The mutual arrangement of the O(2)C(17)C(12)C(13)O(1) and NC(1)C(2) planes is probably fixed by an intramolecular hydrogen bond. In fact, the six-membered heterocycle is not planar; and it is the H-atom that is the most distant from the averaged plane in the first and second molecules (by 0.09 Å and 0.2 Å, respectively).

Fig. 2 presents the projection of the structure on the *xz* plane. The dihydroisoquinoline fragments of the two independent molecules lie in the vicinity of the screw axes; the latter arrange the stacks of molecules along the *y* axis (a stack of molecules of compound **3**, strung around the axis 2 in the 1/2 *y* 1/2 position, is highlighted in Fig. 2). The dimethylcyclohexane «wings» of molecules in both stacks are along the diagonal directions (101). This gives rise to a large number of contacts between those stacks, which are displaced by half the translation along the *z* axis. The layers of stacks thus formed are perpendicular to the *x* axis and come in contact with each other mostly through the atoms of the

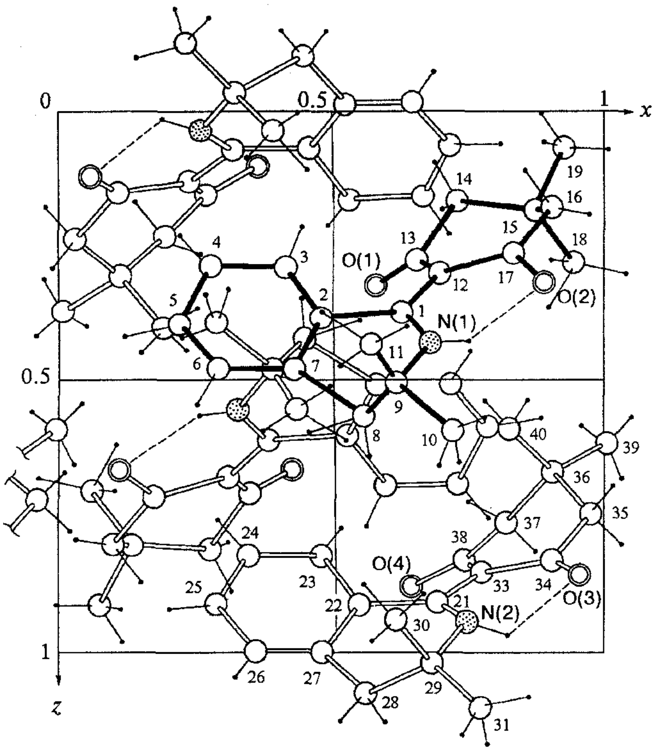


Fig. 2. Projection of the 3,3-dimethyl-1-(4',4'-dimethyl-2',6'-dioxocyclohex-1'-yl)-3,4-dihydroisoquinoline (3) structure onto the *xy* plane.

Table 3. Absorption maxima of some bands in the IR spectra in the region between 4000 cm^{-1} and 1500 cm^{-1}

Compound	Medium	ν (cm^{-1})
1,3,3-Trimethyl-3,4-dihydroisoquinoline (**2**)	Film, KBr Glasses	1602 (CC+CN); 1575 (CC+CN)
5,5-Dimethylcyclohexane-1,3-dione (**1**)	KBr	3682—3269 br (ν_{max} 3549, 3482, 3415) (OH); 1749 (C=O keto form); 1615 (C=O enol form); 1582 (CC+CO); 1562, 1515
	Neat	3000—2500 br (OH); 1621 (enol form, assoc. CO); 1590, 1532 (the «anion band»)[3]
	Neat	1730, 1698 (C=O keto form); 1620, 1585 (C=O enol form)[14]
	Benzene	1733 и 1713* (C=O keto form); 1628 и 1602** (C=O enol form)[3]
	$C_2H_4Cl_2$	1740 и 1714* (C=O keto form); 1655 и 1628** (C=O enol form)[3]
	$CHCl_3$	1733, 1707, 1603[14]
	$CHCl_3$	1734, 1709, 1610[14]
	CCl_4	1737, 1715, 1597[14]
	MeCN	1735, 1714, 1652, 1624***(see ref.[3])
	Dioxane	1738, 1714, 1657, 1623***(see ref.[3])
	Dioxane	1732, 1710, 1645, 1609***(see ref.[3])
	n-$C_{10}H_{21}OH$	1630, 1600 (enol form)[3]
3,3-Dimethyl-1-(4′,4′-dimethyl-2′,6′-dioxocyclohex-1′-yl)-3,4-dihydroisoquinoline (**3**)	KBr	3427 (NH); 1642 (C=O, $A = 5.97 \cdot 10^4$ kg mol^{-1} cm^{-2}); 1609, 1590, 1576, 1544
	CCl_4	3424 (NH); 1642 (C=O, $A = 3.39 \cdot 10^4$ L mol^{-1} cm^{-2})
3-Methyl-1-(4′,4′-dimethyl-2′,6′-dioxocyclohex-1′-yl)-3,4-dihydroisoquinoline (**4**)	KBr	3413 (NH); 1632 (C=O, $A = 4.93 \cdot 10^4$ kg mol^{-1} cm^{-2}); 1608, 1587, 1568, 1547
	CCl_4	3429 (NH); 1643 (C=O, $A = 2.97 \cdot 10^4$ L mol^{-1} cm^{-2})

* More intensive bands.

** Less intensive bands.

*** Intensities of all bands are equal.

dimethylcyclohexane «wings». All the contacts between the molecules are of the normal Van der Waals type.

In the IR and UV spectra the structural features of compound **3** are reflected in the following.

It is known[3,13,14] that absorption bands in the range between 1800 cm^{-1} and 1500 cm^{-1} refer to composite frequencies ν(CO+CC) in the spectra of cyclic β-diketones and to composite frequencies ν(CC+CN) in the spectra of N-containing aromatic heterocyclic compounds. However, owing to the incomplete electron density equalization in the system of conjugated bonds, the high-frequency absorption bands may be attributed, as a first approximation, mainly to the ν(C=O) vibrations, and the low-frequency bands are assigned to ν(C=C) vibrations.

The IR spectrum of a polycrystalline sample of compound **3** (Table 3) exhibits only one ν(C=O) band, which confirms the equivalence of the two carbonyl groups as well as the relatively low stability of the intramolecular hydrogen bond. The displacement of the above-mentioned absorption band to lower frequencies (in relation to the C=O stretching frequencies of the keto tautomer in dimedone) points to conjugation between the C=O group and the heterocyclic moiety.[13–15] The band displacement ($\Delta\nu$) amounts to 40—90 cm^{-1}, i.e., it is somewhat larger than the displacement caused by conjugation with one C=C double bond in position 2, which is usually within 20—30 cm^{-1} (see ref.[13]). The integral intensity, *A*(C=O), in β-diketones is[13] 1.2—4.104 kg mol^{-1} cm^{-2}, and the highest *A*(C=O) values are observed in conjugated systems. Thus, the ν(C=O) and *A*(C=O) values obtained for a sample of **3** in KBr disks (Table 3) indicate substantial conjugation between the rings.

For the reasons discussed above the assignment of the absorption bands in the range between 1600 cm^{-1} and 1540 cm^{-1} to any certain vibration mode is impossible. It is to be noted, however, that the slight symbatic upward frequency shift of these bands in the spectrum of **3** as compared to the bands in the spectrum of 1,3,3-trimethyl-3,4-dihydroisoquinoline is characteristic of protonated heterocycles.[16]

The transformation of the cyclohexane fragment of the molecule to the anion-like form gives rise to a novel

Table 4. Maximum positions and relative intensities of the bands in the UV spectra of compounds

Compound	Solvent	λ (nm) (lg ε)				
Isoquinoline	Cyclohexane	313(3.26),	265(3.62),	218(4.80)[12]		
	Hexane	317(3.49),	266(3.61),	217(4.57)[15]		
1,3,3-Trimethyl-3,4-dihydroisoquinoline (**2**)	EtOH	286,	254,	216		
	MeCN	286,	252,	218		
	Hexane	280,	249,	(213)		
5,5-Dimethylcyclohexane-1,3-dione (**1**)	EtOH		259(4.24)			
	MeCN		248(4.15)			
	H^+(EtOH, 1*M* HCl)		256(4.33)			
	OH^-(EtOH, 1*M* NaOH)		282(4.51)			
3,3-Dimethyl-1-(4′,4′-dimethyl-2′,6′-dioxocyclohex-1′-yl)-3,4-dihydroisoquinoline (**3**)	In KCl pellets	358,	312,	259,	216	
	EtOH	370(3.90),	321(3.62),	265(4.22),	226(3.53)	
	MeCN	373(3.00),	311(3.66),	259(4.29)		
	Acetone	370(3.99)				
	CCl_4	369(3.94),	318(3.69),	263(4.29)		
	DMF	365(4.24),	314(3.97)			
	H^+(EtOH, 1*M* HCl)	—	321(3.73),	291(3.85),	259(4.17)	
	OH^-(EtOH, 1*M* NaOH)	—	—	287(4.20),	264(4.23),	215(3.94)
3-Methyl-1-(4′,4′-dimethyl-2′,6′-dioxocycloxex-1′-yl)-3,4-dihydroisoquinoline (**4**)	EtOH	366(3.92)	318(3.64),	266(4.24),	219(3.53)	
	CCl_4	372(3.94)	291(3.73),	238(4.31)		
	H^+(EtOH, 1*M* HCl)	—	316(3.51),	291(3.73),	257(3.97)	
	OH^-(EtOH, 1*M* NaOH)	—	—	284(4.28),	265(4.09),	213(3.53)

absorption band in the long-wavelength region of the UV spectrum of crystalline **3** in comparison with the spectra of 1,3,4-trimethyl-3,4-dihydroisoquinoline and dimedone (Table 4). The red shift of this band relative to the long-wavelength band in the spectrum of the dimedone anion implies conjugation between the isoquinoline and cyclohexane systems.

Since the IR and UV spectra of compound **4** are practically identical to those of **3**, we assume that both of these compounds have similar molecular structures in the crystalline state.

It has been shown previously that the type of solvent exerts a considerable effect on the position of the tautomeric equilibrium of dimedone. We have studied the tautomerism and the physico-chemical properties of **3** and **4** in various solutions by IR, UV, and NMR (^{13}C and ^{1}H) spectroscopy. It has been found that in aprotic solvents, as in crystals, these compounds exist almost exclusively in the form of the **3b** tautomer. In fact, the IR spectra of these compounds in CCl_4 at a concentration of 10^{-3} *M* in 10—50 mm cell exhibit only one ν(C=O) band whose frequency and integrated intensity are practically identical to those of the band observed for crystalline compounds (see Table 3). The bands corresponding to the nonconjugated keto tautomer of dimedone can not be detected in the 1750—1690 cm^{-1} range even on heating the solution to 50°C.

In the UV spectra of compounds **3** and **4** in CCl_4 the maxima of the long-wavelength transition bands shift bathochromically in respect to the long-wavelength bands in the spectra of 1,3,3-trimethyl-3,4-dihydroisoquinoline and dimedone or to that of the dimedone anion (Table 4). As stated above, this points to the maintainance of conjugation between the two rings and, consequently, to the fact that the conformation of the molecule remains unchanged upon transition from the crystal to a solution in an aprotic solvent.

In the ^{13}C NMR spectra of both compounds, atoms C(12) and C(13) of the carbonyl groups are equivalent; their chemical shift (196.89 ppm) is smaller than that of the C=O group carbon atom (203.4 ppm), but larger than that for the C—OH group (190.2 ppm) of the dimedone molecule.[17] Chemical shifts of the C(16), C(15), and C(14) atoms are also higher than those for the enol tautomer of dimedone and lower than those for the keto form.

The ^{1}H NMR spectra of compound **3** in C_6D_6 indicate the equivalence of the protons attached to the C(16) and C(14) atoms as well as the equivalence of the methyl groups in the cyclohexane fragment. Thus, both the π-interaction between the rings and the intramolecular H-bond are weak, and so around the C(1)—C(12) bond there occurs the rotation of one ring system relative to the other.

In the ^{13}C NMR spectra there are very weak signals at 214.99 ppm and 187.39 ppm, which can be assigned, respectively, to the C=O and the C—OH carbon atoms of the enol tautomer **3c**. The concentration of the enol tautomer in solution evaluated by the ratio of integral intensities of the above signals is not higher than 5 %, which is close to the sensitivity limit of the method.

A similar conclusion can be drawn from the ^{1}H NMR spectra, which exhibit very weak signals of the Me groups in the enol tautomer. The intensity ratio between these signals and the signals of the Me groups of tautomer **3b** is 2:98.

Proton-donating and proton-accepting solvents, which are capable of forming rather strong intermolecular H-bonds, shift the tautomeric equilibrium in dimedone towards the OH form. In contrast to dimedone, for compounds **3** and **4** in such solvents we have observed only conformational changes without any noticeable shift of the tautomeric equilibrium. In fact, the bands in the range between 1750 cm^{-1} and 1620 cm^{-1} are missing from the IR spectra of **3** in MeCN and dioxane solutions, in contrast to those recorded in KBr disks and in CCl_4. The increase in the planarity of the molecule tends to strengthen the π-interaction between the rings. As mentioned above, the ν(C=O) band must move, as a consequence, to lower frequencies. When the planarity of the molecule decreases, the observed absence of absorption bands in the region of 1750—1620 cm^{-1} can be explained primarily by the increase in the angle between the rings along the C(1)—C(12) axis resulting from replacing the intramolecular H bond by stronger bonds between the solute and the solvent. In this case the cyclohexane fragment must correspond in a greater measure to the dimedone anion. The displacement of the absorption band at 1532 cm^{-1} to lower frequencies confirms this assumption, since it is known[3] that the absorption band of the dimedone anion appears at 1532 cm^{-1}.

The data of the UV absorption spectra obtained with solutions (see Table 4) are also consistent with this assumption. The position of the long-wavelength band should be very sensitive to a change in the conformation of the molecule. However, Table 4 indicates that there is no correlation between the position of the band and such properties as polarity (dipole moment, dielectric constants, etc) and acidity (empirical *Z*, *Y* parameters) of the solvents.[12] This is probably due to the fact that the conformational change affects the position of the long-wavelength band maximum simultaneously in two opposite ways. The decrease in the extent of π-interaction between the rings resulting from an increase in the rotation angle, involves a hypsochromic shift, whereas, as the cyclohexane fragment approaches the anion state, the band shifts bathochromically.[18] Therefore, the overall effect depends on the nature of the hydrogen bonds (N—H···A or C—O···H—A) and on the angle of rotation. Examination of the IR and UV spectral data for compound **3** in CCl_4 and MeCN solutions shows that the molecules of compound **3** are more planar in acetonitrile than in CCl_4 or in the crystalline state.

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