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DIBENZODIAZEPINES IN REACTIONS OF 2-ACETYL-DIMEDONE WITH 3,4-DIAMINOBENZOPHENONE

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The reactions of 2-acetyldimedone and 2-acetyl-3-methoxy-5,5-dimethylcyclohex-2-en-1-one with 3,4-diaminobenzophenoneproduce2-[1-(2-amino-5-benzoylphenyl)amino]ethylidene-5,5-dimethyl-1,3-cyclohexanedioneand 2-acetyl-3-(2-amino-5-benzoylphenyl)amino-5,5-dimethylcyclohex-2-en-1-one, which are cyclized by the action of hydrochloric acid, yielding the respective hydrochlorides of 8-benzoyl- and 7-benzoyl-3,3,11-trimethyl-2,3,4,5-tetrahydro-1H-dibenzo[b,e][1,4]diazepin-2-ones. Hydrolytic cleavage of the 8-benzoyl derivative leads to 2-acetyl-3-(2-amino-4-benzoylphenyl)amino-5,5-dimethylcyclohex-2-en-1-one. A similar cleavage to form 2-acetyl-3-(2-aminophenyl)amino-5,5-dimethylcyclohex-2-en-1-one is observed for the known hydrochloride of 3,3,11-trimethyl-2,3,4,5-tetrahydro-1H-dibenzo[b,e][1,4]diazepin-2-one. The structures of the products were confirmed by PMR spectra and x-ray diffraction data.

Condensed systems including the 1,4-diazepine ring are attracting attention because of their diverse and unexpected conversions [1-4]. Continuing our systematic studies of the synthesis of diazepines in reactions of 2-acetyl-1,3-cyclanediones with o-phenylenediamine [5-10], we have studied the interaction of 2-acetyldimedone I and its enol ether II, obtained in accordance with [11], with 3,4-diaminobenzophenone III.

It was shown previously [12-16] that the reactions of 2-acetyl-1,3-cyclanediones and their enol ethers (2-acetyl-3-methoxycyclohex-2-en-1-ones) with nitrogen-containing nucleophiles are regiospecific and are accomplished in the first case through the acetyl carbonyl and in the second case through the trigonal $C_{(3)}$ atom. The presence of two potential reaction centers in the nonsymmetric diamine III suggests the possibility of forming two isomeric condensation products in reactions with either 2-acetyldimedone I or its enol ether II. A simplified evaluation of the reactivities of the amino groups of the diamine III indicates that the course of the reaction through the 3-amino group is always more favorable. And in fact, as a result of the two possible reactions, we obtained only a single product in each case. These were, respectively, 2-[(2-amino-5-benzoylphenyl)amino]ethylidene-5,5-dimethyl-1,3-cyclohexanedione (IV) and 2-acetyl-3-(2-amino-5-benzoylphenyl)amino-5,5-dimethylcyclohex-2-en-1-one (V) (see Scheme).

Treatment of the enamines IV and V with hydrochloric acid leads to the diazepine salts VI and VII, respectively. We found that these diazepine salts, upon treatment with bases under relatively mild conditions, are cleaved at the $N-C_{(7)}$ bond. With such treatment, the diazepine salt VI forms 2-acetyl-3-(2-amino-4-benzoylphenylamino)-5,5-dimethylcyclohex-2-en-1-one (VIII), whereas treatment of the salt VII gives the original enamine V. Such cleavage also occurs in the case of the diazepine salt XII, obtained either from the enamine XI by a procedure given in [9] or by the action of hydrochloric acid on acetyl-3-(2-aminophenyl)amino-5,5-dimethylcyclohex-2-en-1-one (X), which we had synthesized from the enol ether II and o-phenylenediamine. Treatment of the diazepine salt XII with $NaHCO_3$ is also accompanied by rupture of the $N-C_{(7)}$ bond and formation of the enamine X.

The structures of all of the synthesized compounds were confirmed by a combination of spectrometric data and elemental analysis.

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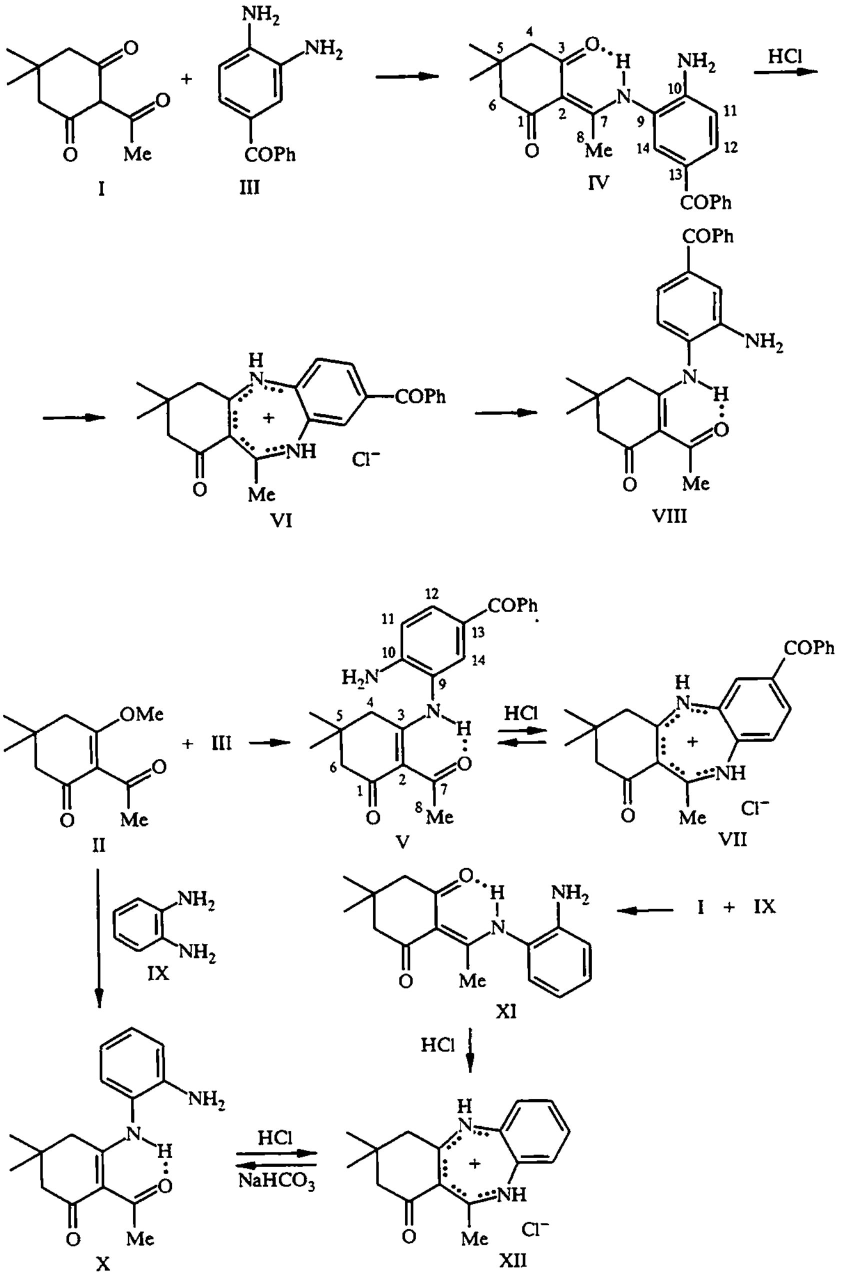
Scheme



In the IR spectra of all the enamines that were obtained (IV, V, VIII, X, XI), we observed two rather intense absorption bands at 3478-3426 and 3370-3338 cm^{-1}, corresponding to stretching vibrations of the NH of the primary amino group. Manifested at lower frequencies is a broad and less-intense band due to stretching vibrations of NH of the secondary amino group of the H-chelate ring. The higher-frequency position of this band (ν_{NH} 3240-3245 cm^{-1}) in the IR spectra, as well as the downfield signal shift of the NH-chelate proton (δ_{NH} 13.6-13.8 cm^{-1}) in the PMR spectra of the enamines (V, VIII, X) in comparison with the 2-(1-aminoethylidene) derivatives (IV, XI) (ν_{NH} 3234-3225 cm^{-1} and δ_H 14.6-14.5 ppm), suggest that the latter are characterized by a stronger intramolecular hydrogen bond.

There is no absorption in the 3400-3200 cm^{-1} region of the IR spectra of the salts; but instead of this absorption, we observe a broad, intense band in the 2700-3000 cm^{-1} region corresponding to ^{+}NH absorption.

All of the synthesized compounds absorb strongly in the 1650-1500 cm^{-1} region, and this characterizes them as systems with an extended $p-\pi$ conjugation chain.

TABLE 1. ^{13}C NMR Chemical Shifts (ppm) and Magnitudes of Direct $^{15}N-^{1}H$ SSCC (Hz) of Compounds IV, V, VIII, X, and XI in Deuterochloroform Solutions

Compound	$C_{(1)}$	$C_{(3)}$	$C_{(2)}$	$C_{(4,6)}$	$C_{(5)}$	$C_{(2Me)}$	$C_{(7)}$	$C_{(8)}$	$C_{(COPh)}$	$C_{(11)}$*	$^{1}J(^{15}N_{(NH2)},H)$	$^{1}J(^{15}N_{NH)},H)$
IV	196,8	200,2	109,0	52,2, 53,6	30,1	28,3	174,5	19,7	194,4	115,0	86,1	85,7
V	172,7	194,8	109,2	51,2, 41,1	30,8	27,9	201,5	32,5	194,3	114,9	86,6	87,6
VIII	172,4	194,9	109,1	52,3, 41,2	30,9	27,9	201,7	32,6	195,8	117,2	82,9	87,5
X	173,0	194,9	108,9	52,3, 40,9	32,6	27,9	201,4	30,8		116,1	81,4	88,1
XI	196,6	199,8	108,6	52,1, 53,4	30,0	28,2	174,4	19,6		116,1	82,0	86,1
XII	182,7	194,3	108,7	50,3, 45,3	29,4	27,2	185,4	25,3				

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*Signals of other aromatic carbon atoms $C_{(9)}$, $C_{(10)}$, $C_{(12)}$, and $C_{(23)}$ are observed in the interval 118.3-146.9 ppm.

TABLE 2. Bond Lengths in Molecules of Compounds X and VIII

Bond	Molecule X	Molecule VIII	Bond	Molecule X	Molecule VIII
$C_{(3)}—N_{(1)}$	1,319(4)	1,338(3)	$C_{(10)}—C_{(9)}$	1,394(4)	1,400(4)
$C_{(3)}—C_{(2)}$	1,412(4)	1,411(4)	$C_{(11)}—C_{(12)}$	1,374(5)	1,371(4)
$C_{(3)}—C_{(4)}$	1,498(5)	1,502(4)	$C_{(11)}—C_{(10)}$	1,373(5)	1,395(4)
$C_{(2)}—C_{(7)}$	1,444(4)	1,458(4)	$C_{(13)}—C_{(14)}$	1,386(5)	1,375(4)
$C_{(2)}—C_{(1)}$	1,454(4)	1,448(4)	$C_{(7)}—O_{(2)}$	1,247(4)	1,231(4)
$C_{(1)}—O_{(1)}$	1,239(4)	1,221(4)	$C_{(7)}—C_{(8)}$	1,516(5)	1,504(4)
$C_{(6)}—C_{(1)}$	1,494(5)	1,503(5)	$C_{(12)}—C_{(17)}$	—	1,490(4)
$C_{(6)}—C_{(5)}$	1,519(5)	1,521(5)	$C_{(17)}—O_{(3)}$	—	1,225(3)
$C_{(5)}—C_{(4)}$	1,519(5)	1,522(4)	$C_{(17)}—C_{(18)}$	—	1,486(4)
$C_{(5)}—C_{(16)}$	1,531(6)	1,529(5)	$C_{(18)}—C_{(23)}$	—	1,383(4)
$C_{(5)}—C_{(15)}$	1,537(6)	1,515(5)	$C_{(18)}—C_{(19)}$	—	1,386(4)
$C_{(9)}—C_{(10)}$	1,372(4)	1,402(4)	$C_{(19)}—C_{(20)}$	—	1,388(6)
$C_{(9)}—C_{(14)}$	1,382(4)	1,384(4)	$C_{(20)}—C_{(21)}$	—	1,361(6)
$C_{(9)}—N_{(1)}$	1,438(4)	1,430(3)	$C_{(21)}—C_{(22)}$	—	1,356(6)
$C_{(10)}—N_{(2)}$	1,388(4)	1,361(4)	$C_{(22)}—C_{(23)}$	—	1,384(5)

As a result of the reactions that were carried out, we had at our disposal three isomeric enamines (IV, V, VIII) obtained on the base of 2-acetyldimedone and 3,4-diaminobenzophenone, and also two isomeric enamines (X, XI) synthesized on the base of 2-acetyldimedone and o-phenylenediamine. Compounds of such a type are potentially tautomeric and may exist in solution in several tautomeric forms [17, 18]. At the same time, our measurements of the SSCC $^1J_{(^{15}N,^1H)}$ show that, the same as in 3-amino-2-acetylcyclohexen-2-ones [17] and N-monosubstituted 2-aminomethyleneindandiones [19], the magnitude of the spin–spin coupling constant in the enamines that we obtained is within a range of values ($^1J_{(^{15}N,^1H)}$ 85.7-88.1 Hz) close to their maximum [20]. Hence we can consider as a proven fact that the H-chelate proton is localized on the $N_{(7)}$ nitrogen atom (as is shown in the Scheme), thereby eliminating the need for examining other possible tautomeric forms.

A characteristic feature of the PMR spectra of the enamines we obtained is that the chemical shifts of the methylene protons $C_{(6)}$ and $C_{(4)}$, of both the 2-(1-aminoalkylidene) derivatives and the 3-amino-2-acetyl derivatives, are very similar, with differences no greater than 0.05 ppm. At the same time, the resonance absorption of the protons of the primary amino group (δ_{NH2} 3.85-4.44 ppm) is determined to a great degree by the presence and location of the benzoyl group in the aromatic ring. Here, the downfield shift of δ_{NH2} of the signal proceeds in the following order: X, XI (δ_{NH2} 3.85 and 3.87 ppm) → VIII (δ_{NH2} 4.06 ppm) → IV, V (δ_{NH2} 4.35 and 4.44 ppm). The signals of the protons of the methyl groups $C_{(8)}$ (δ_{CH3} 2.48 and 2.46 ppm) in the 2-(1-aminoalkylidene) derivatives (IV, XI) are located in stronger fields in comparison with the enamines V, VIII, X (δ_{CH3} 2.59 and 2.62 ppm).

Still another distinctive feature of the PMR spectra of compounds IV and V, which have a benzoyl group in the $C_{(13)}$ position, is the doublet (^3J 8.72 and 8.40 Hz) pertaining to the proton $C_{(11)}H$, standing considerably apart from the other aromatic signals (δ 6.84 and 6.86 ppm). In the spectrum of compound VIII, which has the substituent in position $C_{(12)}$, the signal of this proton is shifted downfield (δ 7.27 ppm) and is a doublet with SSCC 1.3 Hz.

In the ^{13}C NMR spectra, the most highly informative with regard to structure is the resonance signal of the $C_{(11)}$ carbon atom, which, when registered without proton decoupling, has the form of a multiplet, for which the character of splitting also makes it possible to establish reliably the position of the substituent in the aromatic ring. Thus, in compounds X (with no substitution), the signal of the $C_{(11)}$ carbon is a doublet of quartets with spin–spin coupling constants (SSCCs) $^1J_{(^{13}C,^1H)}$ = 157.2 and $^3J_{(^{13}C,^1H)}$ = 6.6 Hz. It is known [21] that in aromatic compounds, the vicinal SSCCs ($^3J_{(^{13}C,^1H)}$ 5-10 Hz) are generally much greater than the geminal constants; therefore, we can consider that this last multiplet is due mainly to spin–spin coupling with protons of the primary amino group and a proton located on the $C_{(13)}$ carbon. This sort of splitting is also observed in compound VIII, thus proving the presence of the substituent at the $C_{(12)}$ atom. In compounds IV and V, where there is a substituent at the $C_{(13)}$ atom, the signal of the $C_{(11)}$ carbon is a double triplet ($^1J_{(^{13}C,^1H)}$ ~ 159.1 and $^3J_{(^{13}C,^1H)}$ = 4.4 Hz), converted by deuterium replacement of the protons of the primary amino group to a doublet with $^1J_{(^{13}C,^1H)}$ = 159.1 Hz with a signal half-width on the order of 2.5 Hz.

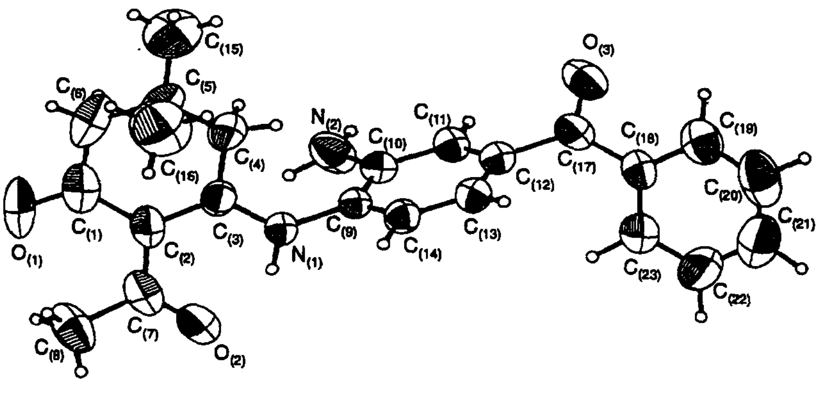

Fig. 1. Three-dimensional model of molecule of VIII, with identification of atoms and ellipsoids of thermal oscillations.

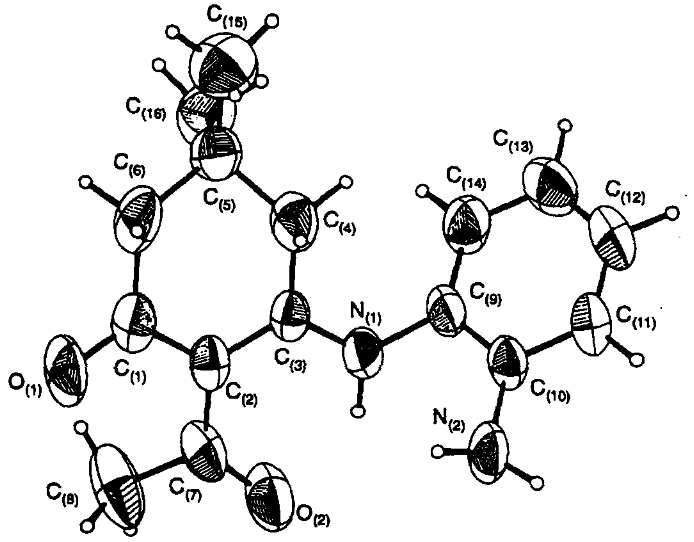

Fig. 2. Three-dimensional model of molecule of X, with identification of atoms and ellipsoids of thermal oscillations.

A comparative analysis of the ^{13}C NMR spectrometric data (Table 1) for the 2-(1-aminoethylidene) derivatives IV and X with those for the enamines V, VIII, and XI shows that the introduction of the amino function into the $C_{(3)}$ position is accompanied by a substantial upfield shift of the $C_{(3)}$ and $C_{(4)}$ signals and a similar downfield shift of the $C_{(7)}$ and $C_{(8)}$ signals; here, the chemical shifts of these carbons atoms are sufficiently characteristic and will also serve for identification of these compounds.

For conclusive proof of the structures of compounds VIII and X, we used data obtained by x-ray diffraction analysis of crystals of these substances. In Figs. 1 and 2 we show three-dimensional models of the molecules of VIII and X, with identification of the atoms. In Tables 2 and 3 we have listed values for the bond lengths and angles in molecules VIII and X. In both structures we find a strong intramolecular hydrogen bond $N_{(1)}-H_{(N1)}\ldots O_{(2)}$. The length of this bond is 2.594(4) Å [$H_{(N1)}\ldots O_{(2)}$ = 1.88(3) Å and $N_{(1)}-H_{(N1)}\ldots O_{(2)}$ = 137(3)°] in the molecule of X, and 2.572(3) Å [$H_{(N1)}\ldots O_{(2)}$ = 1.78(3) Å, $N_{(1)}-H_{(N1)}\ldots O_{(2)}$ = 142(3)°] in the molecule of VIII. Thanks to this bond, still another six-membered H-chelate ring is formed in the molecules, consisting of $O_{(2)}$, $C_{(7)}$, $C_{(3)}$, $C_{(1)}$, $N_{(1)}$, and $H_{(N1)}$; this ring is practically coplanar with the dimedone fragment $C_{(1)}$, $C_{(2)}$, $C_{(3)}$, $C_{(4)}$, $C_{(6)}$. The $C_{(5)}$ atom deviates from this plane by 0.691(4) and 0.687(4) Å in the molecules of VIII and X, respectively. Relative to this plane, the plane of the ring $C_{(9)}$, $C_{(10)}$, $C_{(11)}$, $C_{(12)}$, $C_{(13)}$, $C_{(14)}$ is rotated around the $N_{(1)}-C_{(9)}$ bond by an angle of 70.0(1)° in X. In the molecules of VIII, this angle is 108.3(1)°. These large angles reflect the position of the amino group in the ortho position of the ring, preventing coplanarity of these fragments. The large angles

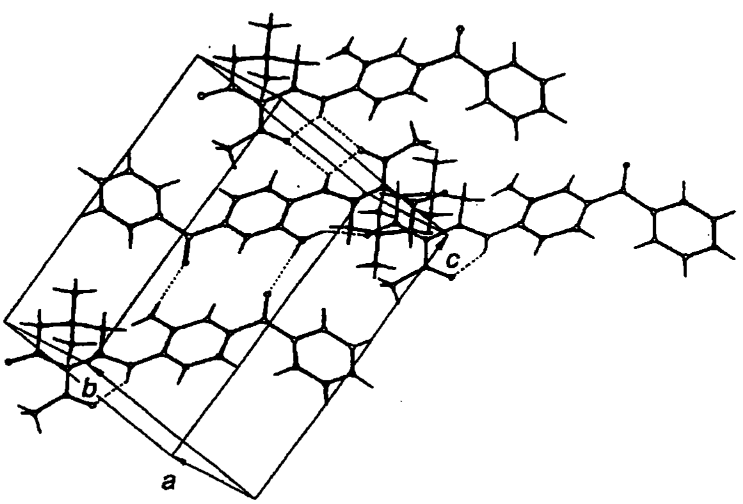

Fig. 3. Elementary cell of crystal and system of hydrogen bonds of compound VIII.

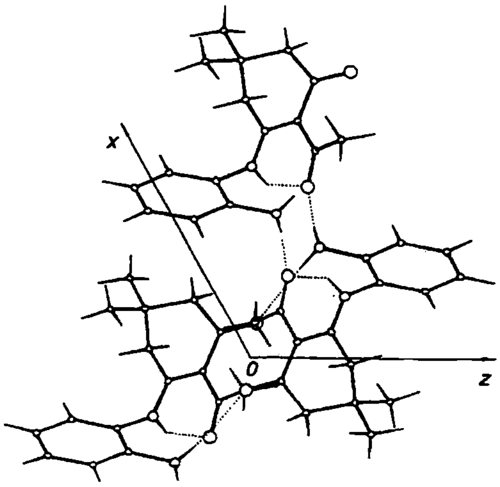

Fig. 4. Fragment of projection of crystallographic structure of compound X onto (010) plane, with an indication of hydrogen bonds.

of rotation of the planes contribute to a breakdown of conjugation in the system. In this connection, the length of the $C_{(9)}-N_{(1)}$ bond (Table 2) is substantially greater than that of the $C_{(3)}-N_{(1)}$ bond. In the molecule of VIII, the dihedral angle between the aromatic ring $C_{(9)}$, $C_{(10)}$, $C_{(11)}$, $C_{(12)}$, $C_{(13)}$, $C_{(14)}$ and the plane of the fragment $O_{(3)}$, $C_{(17)}$, $C_{(12)}$, $C_{(18)}$ is 39.0(1)°, while the dihedral angle between the latter plane and the phenyl ring $C_{(18)}$, $C_{(19)}$, $C_{(20)}$, $C_{(21)}$, $C_{(22)}$, $C_{(23)}$ is 24.9(2)°. The relatively low values of these angles allow a partial preservation of conjugation, and the $C_{(12)}-C_{(17)}$ and $C_{(17)}-C_{(18)}$ bonds can be regarded as sesquivalent.

In the molecule of VIII we observe substantial vibrational thermal oscillations of the $C_{(15)}$ and $C_{(16)}$ atoms (the components of the tensors of thermal parameters for VIII and X will be provided by the authors upon request), and this is responsible for a certain shortening of the lengths of the bonds $C_{(5)}-C_{(15)}$ and $C_{(5)}-C_{(16)}$ [22]. The other values of the bond length are close to the standard values [23].

In addition to the intramolecular hydrogen bond that was discussed in the foregoing material, the crystal structure of compounds VIII and X includes a system of intermolecular hydrogen bonds. The characteristics of these bonds are given in Table 4. In the crystalline compound X, by means of the hydrogen bonds $N_{(2)}-H_{(1,N2)}\cdots O_{(1)}$ and $N_{(2)}-H_{(2,N2)}\cdots O_{(2)}$, chains are formed, parallel to the [221] crystallographic direction.

TABLE 3. Bond Angles in Molecules of Compounds X and VIII

Angle	Molecule X	Molecule VIII	Angle	Molecule X	Molecule VIII
$N_{(1)}—C_{(3)}—C_{(2)}$	121,9(3)	122,0(3)	$N_{(2)}—C_{(10)}—C_{(11)}$	120,7(3)	121,4(3)
$N_{(1)}—C_{(3)}—C_{(4)}$	118,1(3)	115,9(2)	$C_{(12)}—C_{(11)}—C_{(10)}$	121,4(3)	122,4(3)
$C_{(2)}—C_{(3)}—C_{(4)}$	120,0(3)	122,1(3)	$C_{(13)}—C_{(12)}—C_{(11)}$	120,2(3)	119,6(3)
$C_{(3)}—C_{(2)}—C_{(7)}$	120,6(3)	119,1(3)	$C_{(11)}—C_{(12)}—C_{(17)}$	—	119,4(3)
$C_{(3)}—C_{(2)}—C_{(1)}$	118,2(3)	118,3(3)	$C_{(13)}—C_{(12)}—C_{(17)}$	—	121,0(3)
$C_{(7)}—C_{(2)}—C_{(1)}$	121,2(3)	122,0(3)	$C_{(12)}—C_{(13)}—C_{(14)}$	118,9(3)	119,4(3)
$O_{(1)}—C_{(1)}—C_{(2)}$	122,7(3)	123,8(4)	$C_{(9)}—C_{(14)}—C_{(13)}$	120,8(4)	120,7(3)
$O_{(1)}—C_{(1)}—C_{(6)}$	118,0(3)	117,5(3)	$O_{(2)}—C_{(7)}—C_{(2)}$	122,0(3)	121,5(3)
$C_{(2)}—C_{(1)}—C_{(6)}$	119,4(3)	118,7(3)	$O_{(2)}—C_{(7)}—C_{(8)}$	117,1(4)	117,0(4)
$C_{(1)}—C_{(6)}—C_{(5)}$	116,8(3)	114,5(3)	$C_{(2)}—C_{(7)}—C_{(8)}$	120,8(4)	121,4(4)
$C_{(4)}—C_{(5)}—C_{(6)}$	106,4(3)	106,1(3)	$O_{(3)}—C_{(17)}—C_{(18)}$	—	120,4(3)
$C_{(4)}—C_{(5)}—C_{(16)}$	108,7(4)	108,4(3)	$O_{(3)}—C_{(17)}—C_{(2)}$	—	119,7(3)
$C_{(6)}—C_{(5)}—C_{(16)}$	110,3(3)	110,6(3)	$C_{(18)}—C_{(17)}—C_{(2)}$	—	119,9(3)
$C_{(4)}—C_{(5)}—C_{(15)}$	110,6(3)	111,9(3)	$C_{(23)}—C_{(18)}—C_{(19)}$	—	118,2(3)
$C_{(6)}—C_{(5)}—C_{(15)}$	110,3(4)	110,7(3)	$C_{(23)}—C_{(18)}—C_{(17)}$	—	122,5(3)
$C_{(16)}—C_{(5)}—C_{(15)}$	110,4(4)	109,0(4)	$C_{(19)}—C_{(18)}—C_{(17)}$	—	119,3(3)
$C_{(3)}—C_{(4)}—C_{(5)}$	113,3(3)	114,7(3)	$C_{(18)}—C_{(19)}—C_{(20)}$	—	120,0(4)
$C_{(10)}—C_{(9)}—C_{(14)}$	120,7(3)	121,1(2)	$C_{(21)}—C_{(20)}—C_{(19)}$	—	120,7(4)
$C_{(10)}—C_{(9)}—N_{(1)}$	118,9(3)	119,6(3)	$C_{(22)}—C_{(21)}—C_{(20)}$	—	120,0(4)
$C_{(14)}—C_{(9)}—N_{(1)}$	120,2(3)	119,2(2)	$C_{(21)}—C_{(22)}—C_{(23)}$	—	120,1(4)
$C_{(9)}—C_{(10)}—N_{(2)}$	121,2(3)	121,8(3)	$C_{(22)}—C_{(23)}—C_{(18)}$	—	120,9(3)
$C_{(9)}—C_{(10)}—C_{(11)}$	118,0(3)	116,7(3)	$C_{(3)}—N_{(1)}—C_{(9)}$	128,2(3)	125,0(3)

TABLE 4. Geometric Characteristics of Intermolecular Hydrogen Bonds in Structures of X and VIII

Bond	Length N...O, Å	Length H...O, Å	Angle NH...O, °	Symmetry of O atom
	Compound X			
$N_{(2)}—H_{(1,N1)}...O_{(2)}$	3,096(4)	2,12(3)	175(3)	$3-x, -1/2+y, 5/2-z$
$N_{(2)}—H_{(2,N2)}...O_{(1)}$	3,054(4)	2,21(4)	162(3)	$2-x, -y, 2-z$
	Compound VIII			
$N_{(1)}—H_{(N1)}...O_{(2)}$	3,029(3)	2,37(3)	128(3)	$1-x, 1-y, 2-z$
$N_{(2)}—H_{(1,N2)}...O_{(3)}$	3,054(4)	2,25(3)	169(3)	$1-x, 1-y, 1-z$

In the crystals of VIII, the system of H-bonds is more highly branched. Along with the intramolecular bond $N_{(1)}-H_{(N1)}\cdots O_{(2)}$, we find an intermolecular bond $N_{(1)}-H_{(N1)}\cdots O_{(2)}$. Thus, the hydrogen atom $H_{(N1)}$ participates in forked H-bonds, one of which is intermolecular and the other intramolecular. Also present in the structure of VIII are the H-bonds $N_{(2)}-H_{(1,N2)}\cdots O_{(1)}$ and $N_{(2)}-H_{(2,N2)}\cdots O_{(3)}$. Through the intermolecular hydrogen bonds, the molecules in the crystal are joined into networks that are parallel to the (100) plane in the crystal lattice. The lengths of these bonds are somewhat greater than the statistical mean value of 2.89 Å given in [24] for H-bonds of the NH...O type. Fragments of the crystal structures of VIII and X with their systems of H-bonds are shown in Figs. 3 and 4.

EXPERIMENTAL

The IR spectra were registered on a Specord 75 instrument, in white mineral oil. The ^1H and ^{13}C NMR spectra were recorded on solutions of the compounds on deuterochloroform, deutero(dimethyl sulfoxide), or a mixture of these solvents, in a Bruker AM-360 spectrometer at frequencies of 360 and 90.52 MHz, respectively, at a temperature of 303 K. The chemical shifts are given relative to TMS. The assignments of the carbon-atom signals were made with an accounting for the character of splitting in the monoresonance spectra, the signal intensities, and the values of the SSCC (^{13}C, ^1H).

TABLE 5. Coordinates of Atoms in Molecule of Compound VIII

Atom	*x*	*y*	*z*
C(3)	0,3009(4)	0,3218(3)	0,9141(2)
C(2)	0,3234(4)	0,2284(3)	1,0088(2)
C(1)	0,2677(4)	0,0959(4)	1,0302(2)
C(6)	0,1846(5)	0,0675(4)	0,9514(3)
C(5)	0,0816(4)	0,2269(4)	0,8766(2)
C(4)	0,2023(5)	0,3030(5)	0,8388(2)
C(9)	0,3426(4)	0,5363(3)	0,7922(2)
C(10)	0,4428(4)	0,4662(3)	0,7210(2)
C(11)	0,4171(4)	0,5743(4)	0,6311(2)
C(12)	0,3048(4)	0,7423(4)	0,6133(2)
C(13)	0,2087(4)	0,8092(4)	0,6860(2)
C(14)	0,2282(4)	0,7055(4)	0,7745(2)
C(7)	0,4055(4)	0,2634(4)	1,0811(2)
C(8)	0,4005(7)	0,1933(7)	1,1851(3)
C(15)	-0,0688(6)	0,3482(6)	0,9190(4)
C(16)	0,0184(7)	0,1830(7)	0,7944(4)
C(17)	0,2822(4)	0,8491(4)	0,5155(2)
C(18)	0,2559(4)	1,0272(4)	0,5019(2)
C(19)	0,1758(5)	1,1421(4)	0,4179(3)
C(20)	0,1515(6)	1,3085(5)	0,4037(3)
C(21)	0,2083(6)	1,3602(5)	0,4708(3)
C(22)	0,2907(5)	1,2484(5)	0,5523(3)
C(23)	0,3132(5)	1,0826(4)	0,5687(2)
N(1)	0,3647(3)	0,4337(3)	0,8861(2)
N(2)	0,5541(4)	0,2995(4)	0,7369(2)
O(2)	0,4757(3)	0,3573(3)	1,0601(1)
O(1)	0,2904(4)	0,0002(3)	1,1080(2)
O(3)	0,2863(3)	0,7891(3)	0,4468(1)
H(N1)	0,425(4)	0,438(4)	0,936(2)
H(2,N2)	0,608(4)	0,267(4)	0,693(2)
H(1,N2)	0,597(4)	0,231(4)	0,799(2)
H(C11)	0,486(4)	0,530(3)	0,583(2)
H(C13)	0,122(4)	0,925(4)	0,673(2)
H(C14)	0,154(3)	0,756(3)	0,831(2)
H(C19)	0,134(4)	1,095(4)	0,376(2)
H(C20)	0,089(6)	1,379(6)	0,345(3)
H(C21)	0,185(5)	1,481(6)	0,462(3)
H(C22)	0,340(5)	1,272(5)	0,600(3)
H(C23)	0,383(5)	1,007(4)	0,623(3)
H(1,C6)	0,260(5)	-0,002(5)	0,910(3)
H(2,C6)	0,117(5)	0,020(5)	0,977(3)
H(1,C4)	0,148(4)	0,410(5)	0,792(3)
H(2,C4)	0,279(5)	0,239(5)	0,793(3)
H(1,C8)	0,294(5)	0,192(4)	1,201(3)
H(2,C8)	0,475(6)	0,071(6)	1,204(3)
H(3,C8)	0,439(6)	0,248(5)	1,223(3)
H(1,C15)	-0,031(6)	0,368(6)	0,978(4)
H(2,C15)	-0,129(6)	0,448(6)	0,869(4)
H(3,C15)	-0,168(7)	0,294(7)	0,948(4)
H(1,C16)	-0,049(5)	0,281(6)	0,745(3)
H(2,C16)	0,123(6)	0,098(6)	0,764(3)
H(3,C16)	-0,060(5)	0,138(5)	0,814(3)

The constants $^1J_{(^{15}N,^1H)}$ were registered in this same spectrometer, on the basis of an inverse method proposed in [25].

Single crystals of compound X, composition $C_{16}H_{20}N_2O_2$, grown from ethanol, monoclinic; space group P $2_{1/c}$. Elementary cell constants: a = 9.682(3), b = 12.682(3), c = 13.743(2) Å, β = 117.58(2)°, V = 1489.4(6) Å^3, Z = 4, F(000) = 548, μ = 0.08 mm^{-1}, D_x = 1.215(1) g cm^{-3}.

Single crystals of compound VIII, composition $C_{23}H_{24}N_2O_3$, grown from methanol, belong to triclinic system, and are characterized by the following crystallographic parameters: a = 8.798(3), b = 9.013(2), c = 14.473(2) Å, α = 77.16(2), β = 87.59(3), γ = 64.18(2)°, V = 1005.3(5) Å^3, Z = 2, F(000) = 400, μ = 0.08 mm^{-1}, D_x = 1.244(1) g cm^{-3}; sp. gp. P-$\bar{1}$.

TABLE 6. Coordinates of Atoms in Molecule of Compound X

Atom	*x*	*y*	*z*
$C_{(3)}$	1,1045(3)	0,0298(2)	1,1981(2)
$C_{(2)}$	1,0608(3)	0,1077(2)	1,1154(2)
$C_{(1)}$	0,8991(4)	0,1114(3)	1,0313(3)
$C_{(6)}$	0,7783(4)	0,0534(4)	1,0492(3)
$C_{(5)}$	0,8266(4)	0,0128(3)	1,1646(3)
$C_{(4)}$	0,9833(4)	-0,0411(3)	1,2022(3)
$C_{(9)}$	1,3121(3)	-0,0565(2)	1,3631(2)
$C_{(10)}$	1,4052(3)	-0,1389(2)	1,3640(2)
$C_{(11)}$	1,4734(4)	-0,2021(3)	1,4577(3)
$C_{(12)}$	1,4473(4)	-0,1839(3)	1,5464(3)
$C_{(13)}$	1,3537(5)	-0,1016(3)	1,5447(3)
$C_{(14)}$	1,2876(4)	-0,0371(3)	1,4528(3)
$C_{(7)}$	1,1750(4)	0,1800(3)	1,1135(2)
$C_{(8)}$	1,1252(7)	0,2797(3)	1,0443(4)
$C_{(15)}$	0,8401(6)	0,1052(5)	1,2413(4)
$C_{(16)}$	0,7090(6)	-0,0690(6)	1,1632(5)
$N_{(1)}$	1,2511(3)	0,0148(2)	1,2711(2)
$N_{(2)}$	1,4381(4)	-0,1554(3)	1,2770(2)
$O_{(2)}$	1,3176(3)	0,1671(2)	1,1731(2)
$O_{(1)}$	0,8564(3)	0,1600(2)	0,9438(2)
$H_{(1,C6)}$	0,679(4)	0,091(3)	1,020(3)
$H_{(2,C6)}$	0,749(4)	-0,011(3)	1,005(3)
$H_{(1,C4)}$	1,023(4)	-0,068(2)	1,273(3)
$H_{(2,C4)}$	0,974(4)	-0,099(3)	1,154(3)
$H_{(N1)}$	1,319(4)	0,051(2)	1,260(2)
$H_{(1,N2)}$	1,511(4)	-0,213(3)	1,289(3)
$H_{(2,N2)}$	1,358(4)	-0,142(3)	1,214(3)
$H_{(C11)}$	1,540(3)	-0,258(2)	1,459(2)
$H_{(C12)}$	1,508(4)	-0,236(3)	1,611(3)
$H_{(C13)}$	1,331(4)	-0,078(3)	1,606(3)
$H_{(C14)}$	1,226(3)	0,019(2)	1,448(2)
$H_{(1,C8)}$	1,212(5)	0,326(3)	1,073(3)
$H_{(2,C8)}$	1,027(6)	0,311(4)	1,043(4)
$H_{(3,C8)}$	1,107(6)	0,258(4)	0,974(4)
$H_{(1,C15)}$	0,734(5)	0,135(3)	1,221(3)
$H_{(2,C15)}$	0,884(5)	0,071(4)	1,315(4)
$H_{(3,C15)}$	0,919(5)	0,159(3)	1,245(3)
$H_{(1,C16)}$	0,609(6)	-0,037(3)	1,131(3)
$H_{(1,C16)}$	0,728(6)	-0,092(4)	1,230(4)
$H_{(1,C16)}$	0,701(6)	-0,128(4)	1,110(4)

The intensities of independent reflections (1964 for X and 2648 for VIII) were measured in a Syntex $P2_1$ automatic four-circle diffractometer (MoKα radiation, graphite monochromator, $\theta/2\theta$ scanning, $2\theta_{max} = 45°$). In the calculations we used 1255 reflections for X and 1765 reflections for VIII with $|F| > 4.0\sigma(F)$. The structures were deciphered by a procedure given in [26] and were refined by full-matrix LSM with anisotropic temperature factors. All of the hydrogen atoms were localized by a difference synthesis and were refined isotropically. The final values of the divergence factor were 0.0546 for the X and 0.0547 for the VIII. In performing the calculations, we used the AREN program set [27]. The coordinates of the atoms in the structures of X and VIII are given in Tables 5 and 6.

2-[1-(2-Amino-5-benzoylphenyl)amino]ethylidene-5,5-dimethyl-1,3-cyclohexanedione (IV). Refluxed 0.46 g (2.5 mmoles) of 2-acetyldimedone and 0.54 g (2.5 mmoles) of 3,4-diaminobenzophenone in 20 ml of ethanol for 0.5 h. The precipitate of IV that was formed during the time of refluxing the reaction mixture was filtered off and recrystallized from ethanol. Yield 0.70 g (74%), mp 168-169°C. IR spectrum: 1635, 1622, 1590, 1580, 1560, 1515, 3478, 3370, 3234 cm^{-1}. PMR spectrum in $CDCl_3$: 1.07 (6H, s, $2CH_3$); 2.41 (2H, s, CH_2); 2.47 (2H, s, CH_2); 2.48 (2H, s, CH_3) 4.35 (2H, br.s, NH_2); 6.84 (1H, d, J = 8.72 Hz; =CH); 7.44-7.51 (3H, m, arom.); 7.69-7.74 (2H, m, arom.); 14.61 (1H, br.s, NH). Found, %: C 73.20; H 6.31; N 7.30. $C_{23}H_{24}N_2O_3$. Calculated, %: C 73.38; H 6.43; N 7.44.

3-(2-Amino-5-benzoylphenylamino)-2-acetyl-5,5-dimethylcyclohex-2-en-1-one (V). *A*. To a solution of 0.49 g (2.5 mmoles) of 2-acetyl-3-methoxy-5,5-dimethylcyclohex-2-en-1-one, obtained in accordance with [16], in 2 ml of anhydrous methanol, a solution of 0.54 g (2.5 mmoles) of 3,4-diaminobenzophenone in 5 ml of anhydrous methanol was added, and the mixture was left for 48 h at 20°C. The resulting precipitate was filtered off and then boiled for 5 min in 30 ml of methanol with activated carbon. Several drops of water were added to the hot filtrate, after which it was cooled. Obtained 0.69 g (73%), mp 199-202°C. This substance gave a depression of melting point with compound IV.

B. To a solution of 0.20 g (0.5 mmole) of the diazepine salt VII in 10 ml of ethanol, 10 ml of a 5% aqueous solution of $NaHCO_3$ was added. The resulting precipitate was filtered off and recrystallized from aqueous ethanol. Yield 0.12 g (63%), mp 194-196°C. Does not give any depression of melting point with a sample of the substance obtained by method A. IR spectrum: 1652, 1635, 1602, 1560, 3425, 3342, 3242 cm^{-1}. PMR spectrum in $CDCl_3$: 1.03 (6H, s, $2CH_3$); 2.31 (2H, s, CH_2); 2.36 (2H, s, CH_2); 2.59 (3H, s, CH_3); 4.44 (2H, br.s, NH_2); 6.86 (1H, d, J = 8.4 Hz, arom.); 7.45-7.58 (5H, m, arom.); 7.69-7.73 (2H, m, arom.); 13.64 (1H, NH). Found, %: C 73.30; H 6.28; N 7.25. $C_{23}H_{24}N_2O_3$. Calculated, %: C 73.38; H 6.43; N 7.44.

Hydrochloride of 3,3,11-Trimethyl-8-benzoyl-2,3,4,5-tetrahydro-1H-dibenzo[b,e][1,4]diazepin-2-one (VI). A 0.38-g quantity (1 mmole) of the enamine IV was dissolved in 40 ml of ethanol and heated to 50-60°C, after which 4 ml of concentrated HCl was added, and the mixture was left in the cold for one day. The bright red crystals that formed were filtered off and washed on the filter with diethyl ether. Yield 0.32 g (81%), mp 247-249°C. IR spectrum: 1600, 1645, 1615, 1605, 1580, 1550, 1520, 2750-2880 cm^{-1}. PMR spectrum in $CDCl_3$ + DMSO: 1.03 (6H, s, $2CH_3$); 2.29 (2H, s, CH_2); 2.54 (3H, s, CH_3); 2.78 (2H, s, CH_2); 7.44 (1H, d, J = 7.9 Hz, arom.); 7.51-7.66 (5H, m, arom.); 7.64 (1H, d.t, J = 7.7 & 1.2 Hz, arom.); 7.72 (2H, m, arom.); 11.73 (1H, br.s, NH); 12.68 (1H, br.s, NH). Found, %: C 69.75; H 5.70; N 7.20; Cl 9.10. $C_{23}H_{23}ClN_2O_3$. Calculated, %: 69.95; H 5.87; Cl 8.98; N 7.09.

Hydrochloride of 3,3,11-Trimethyl-7-benzoyl-2,3,4,5-tetrahydro-1H-dibenzo[b,e][1,4]diazepin-2-one (VII). A 0.38 g (1 mmole) quantity of the enamine V was dissolved in 20 ml of ethanol at 20°C, 2 ml of concentrated HCl was added, and the mixture was left for one day. The precipitated red crystals of the diazepine salt VII were filtered off and washed on the filter with diethyl ether. The filtrate was evaporated in a rotary evaporator at 20°C down to 5-7 ml and then left for another day. The additional crystals of VII that formed were filtered off and washed with diethyl ether. Total yield 0.24 g (61%), mp 232-234°C. This substance gives a depression of melting point with the diazepine salt VI. IR spectrum: 1685, 1665, 1645, 1620, 1590, 1575, 1540, 1520, 2980-2500 cm^{-1}. PMR spectrum in $CDCl_3$ + DMSO: 1.06 (6H, s, $2CH_3$); 2.28 (2H, s, CH_2); 2.64 (5H, s, CH_3 + CH_2); 7.44-7.53 (5H, m, arom.); 7.64 (1H, d.t, J = 7.4 & 1.2 Hz, arom.); 7.72-7.76 (2H, m, arom.); 11.17 (1H, br.s, NH); 13.32 (1H, br.s, NH). Found, %: C 69.75; H 5.70; Cl 9.10; N 7.20. Calculated, %: C 69.95; H 5.87, Cl 8.98; N 7.09.

2-Acetyl-3-(2-amino-4-benzoylphenyl)amino-5,5-dimethyl-1,3-cyclohexanedione (VIII). A suspension of 0.20 g (0.50 mmole) of the diazepine salt VI in 10 ml of water was heated to 60-70°C while stirring, after which stirring was continued at this temperature until the reaction mixture had become completely decolorized. The precipitated of VIII was filtered off and recrystallized from ethanol. Yield 0.15 g (80%), mp 181-183°C. IR spectrum: 1660, 1635, 1605, 1580, 1555, 1510, 3450, 3362, 3245 cm^{-1}. PMR spectrum in $CDCl_3$: 1.02 (6H, s, $2CH_3$); 2.33 (2H, s, CH_2); 2.39 (2H, s, CH_2); 2.62 (3H, s, CH_3); 4.06 (2H, br.s, NH_2); 7.06 (1H, d.d, J = 1.3 & 7.9 Hz, arom.); 7.16 (1H, d.d, J = 7.9 & 1.3 Hz, arom.); 7.27 (1H, d, J = 1.3 Hz, arom.); 7.49 (2H, t, J = 7.3 Hz, arom.); 7.60 (1H, t, J = 7.3 Hz, arom.); 7.81 (2H, d, J = 7.3 Hz, arom.), 13.79 (1H, br.s, NH). Found, %: C 73.5; H 6.30; N 7.26. $C_{23}H_{24}N_2O_3$. Calculated, %: C 73.38; H 6.43; N 7.44.

3-(2-Aminophenyl)amino-2-acetyl-5,5-dimethyl-1,3-cyclohexanedione (X). *A*. To a solution of 0.49 g (2.5 mmoles) of 2-acetyl-3-methoxy-5,5-dimethylcyclohex-2-en-1-one in 2 ml of anhydrous methanol, a solution of 0.27 g (2.5 mmoles) of o-phenylenediamine in 6 ml of anhydrous methanol was added, and the mixture was left for 48 h at 20°C. The solvent was removed in a rotary evaporator, and the residue was recrystallized from dry benzene. Yield 0.59 g (77%), mp 119-120°C.

B. A 0.58-g quantity (2 mmoles) of the diazepine salt X was dissolved in 50 ml of water, after which 10 ml of a 5% aqueous $NaHCO_3$ solution was added slowly in drops over the course of 10 min. The colorless precipitate was filtered off and recrystallized from ethanol. Yield 0.45 g (83%), mp 118-120°C. Samples obtained by the two methods did not exhibit any depression of melting point. IR spectrum: 1660, 1640, 1600, 1578, 1560, 1510, 3420, 3370, 3240 cm^{-1}. PMR spectrum in $CDCl_3$: 0.99 (6H, s, $2CH_3$); 2.31 (2H, s, CH_2); 2.34 (2H, s, CH_2); 2.62 (3H, s, CH_3); 3.85 (2H, br.s, NH_2); 6.77 (1H, d.t, J = 7.4 & 1.3 Hz, arom.); 6.81 (1H, d.t, J = 8.1 & 1.3 Hz, arom.); 6.95 (1H, d.d, J = 7.4 & 1.3 Hz, arom.); 7.17 (1H, d.t, J = 1.3 & 8.1 Hz, arom.); 13.59 (1H; br.s, NH). Found, %: C 70.43; H 7.45; N 10.17 $C_{16}H_{20}N_2O_2$. Calculated, %: C 70.56; H 7.40; N 10.29.

2-[1-(2-Aminophenyl)amino]ethylidene-5,5-dimethyl-1,3-cyclohexanedione (XI) was obtained by a procedure given in [10]. IR spectrum: 1645, 1638, 1605, 1572, 1555, 1510, 3445, 3362, 3225 cm^{-1}. PMR spectrum in $CDCl_3$: 1.07 (6H, s, $2CH_3$); 2.43 (4H, s, $2CH_2$); 2.46 (3H, s, CH_3); 3.87 (2H, br.s, NH_2); 6.74 (1H, d.t, J = 7.4 & 1.3 Hz, arom.); 6.77 (1H, d.d, J = 8.1 & 1.3 Hz, arom.); 6.94 (1H, d.d, J = 8.1 & 1.3 Hz, arom.); 7.11 (1H, d.t, J = 8.1 & 1.3 Hz, arom.); 14.47 (1H, br.s, NH).

Hydrochloride of 3,3,11-Trimethyl-2,3,4,5-tetrahydro-1H-dibenzo[b,e][1,4]diazepin-2-one (XII). To a solution of 0.3 g (1.1 mmoles) of 3-(2-aminophenyl)amino-2-acetyl-5,5-dimethylcyclohex-2-en-1-one in 5 ml of ethanol, 1 ml of concentrated HCl was added, and the solution was left for one day in the cold. The hydrochloride was filtered off and washed on the filter with diethyl ether. Yield of dark red crystals of XII 0.20 g (63%), mp 262-265°C. The sample did not give any melting point depression with a sample of the hydrochloride obtained from 2-[1-(2-aminophenyl)amino]ethylidene-5,5-dimethyl-1,3-cyclohexanedione XI in accordance with [9]. IR spectrum: 1700, 1655, 1620, 1600, 1580, 1540, 1510, 3000-2800 cm^{-1}. PMR spectrum and DMSO: 0.97 (6H, s, $2CH_3$); 2.23 (2H, s, CH_2); 2.43 (3H, s, CH_3); 2.65 (2H, s, CH_2); 7.07 (1H, d.d, J = 7.8 & 1.7 Hz, arom.); 7.09 (1H, d.d, J = 7.8 & 1.7 Hz, arom.); 7.21 (1H, d.t, J = 1.7 & 7.8 Hz, arom.), 7.27 (1H, d.t, J = 7.8 & 1.7 Hz, arom.); 11.17 (1H, br.s, NH).

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