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STUDY OF PRODUCTS OF REACTION OF DIAROYLETHYLENES WITH o-PHENYLENEDIAMINE AND 1,3-DIMETHYL-5,6-DIAMINOURACIL

V. D. Orlov, S. M. Desenko,
B. Insuasti, K. A. Potekhin,
and Yu. T. Struchkov

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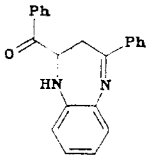
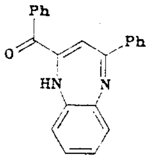
It was shown that the product of the reaction of dibenzoylethylene with o-phenylenediamine has the structure of 2-phenacyl-3-phenyl-1,2-dihydroquinoxaline. The steric structure of the dihydroqyinoxaline bicyclic compound was discussed. It was shown that the reaction of di(4-toluyl)ethylene with 1,3-dimethyl-5,6-diaminouracil leads to 5,7-dimethyl-6,8-dioxo-2-(4-methylphenacylidene)-3-(4-tolyl)-1,2-dihydropyrimidino[5,6-b]pyrazine.

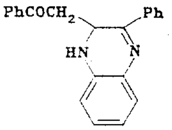
The reactions of o-phenylenediamine with dibenzoylethylene have been dealt with in several contradictory reports [1-6]. This was due first of all to the ambiguous character of the spectral proofs of the proposed sturctures of the compounds formed. In particular, it was difficult to decide between the diazepine [2-4] and quinoxaline [5, 6] structures, corresponding to two alternative paths of cyclocondensation:



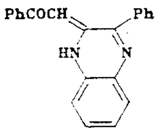
I



II



III



IV

Thus, for one of the compounds obtained in [4], a benzodiazepine structure II was proposed, based on the mass, PMR, IR, and UV spectral data. In a later publication [5], a 2-phenacylidene-3-phenyl-1,2-dihydroquinoxaline structure (IV) was proposed for the same compound, and the only argument refuting structure II was the presence of a carbonyl carbon atom signal with δ 182.4 ppm in the ^{13}C NMR spectrum, whereas the signal of the corresponding carbon nucleus of compound II should be expected in stronger fields. In [5], an intermediate in the formation of compound IV is also described, which can be both oxidized into IV and may split off a molecule of acetophenone to form 2-phenylquinoxaline. Considering these facts and taking also the spectral characteristics of the compound obtained into account, the authors of [5] proposed for it the structure of 2-phenacyl-3-phenyl-1,2-dihydroquinoxaline (III).

A. M. Gor'kii Kharkov State University, Khar'kov 310077. A. N. Nesmeyanov Institute of Heteroorganic Compounds, Moscow 117813. P. I. Lebedev-Polyanskii Vladimir State Pedagogical Institute, Vladimir 600024. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 4, pp. 523-527, April, 1987. Original article submitted December 2, 1986.

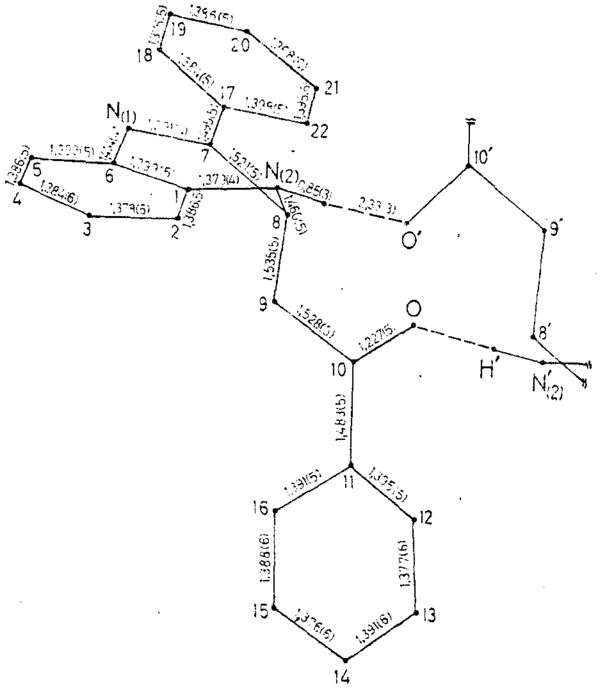


Fig. 1. Structure of molecule of III (of the H atoms, only the H_N is shown) with bond lengths.

The alternative dihydrobenzodiazepine structure I was not considered in [5], although similar chemical and spectral properties could be expected for this compound. The authors of [7] found that the aromatic derivatives of 2,3-dihydro-1H-1,5-benzodiazepine are capable of undergoing intramolecular rearrangements with splitting of a molecule of an acetylarene leading ring contraction. These processes are also observed during mass-spectrometric dissociation, and hence cannot serve as a criterion for choosing between structures I and III.

To solve the problem of the structure of the reaction product of dibenzoylethylene with o-phenylenediamine, we carried out an x-ray diffraction analysis of the compound with mp 124°C [5], which unequivocally showed that this compound has the structure of 2-phenacyl-3-phenyl-1,2-dihydroquinoxaline (III). This indirectly confirmed the fact that the product of its oxidation has structure IV. The geometry of the molecule of III with its bond lengths is shown in Fig. 1. The atomic coordinates and some valence and torsion angles are given in Tables 1-3. The experimental bond lengths correspond completely with the 1,2-dihydroquinoxaline structure, excluding the contribution of the 1,4-dihydrogenated form.

The authors of [6] noted the absence of any IR spectral indications of the existence of hydrogen bonds in compound III in solutions. Coincidentally, the values of ν_{NH} of compound III and its substituted derivatives measured in KBr tablets [6], are on the average lower by 23 cm^{-1} than ν_{NH} of the corresponding 2-aryl-1,2-dihydroquinoxalines. This is due to the fact that the molecules of the compounds studied form in crystals cyclic dimeric H-associates (Fig. 1). Two hydrogen bonds of type N—H···O=C unite the molecules of III into dimers bound by an inversion center. This is indicated by the N···O and H···O distances, equal to 3.121(5) and 2.33(3) Å, respectively. Angle N—H···O is equal to 157(1)°, which is also characteristic of the H bonds. The dimers of compound III appear as one whole unit in the structure of the crystalline lattice. Their existence may be explained by the fact that the unit cell is formed of eight molecules, while for cyrstals of organic compounds in the space group found, in general, Z = 4.

It should also be noted that analysis of a Dreiding model of the molecule of III showed that approach of the oxygen atoms of the carbonyl group and of the imino group hydrogen atom is accompanied by increased screening of the C—H bonds, which probably determines the absence of an intramolecular H bonding both in crystals and in solutions of compound III.

The conformation of the dihydroquinoxaline ring is close to "convert." Thus, the $N_{(1)}$—$C_{(6)}$—$C_{(1)}$—$N_{(2)}$ and $C_{(6)}$—$N_{(1)}$—$C_{(7)}$—$C_{(8)}$ fragments are practically planar (see Table 3). The $C_{(7)}$ atom deviates from the plane of the annelated benzene ring inappreciably (by 0.10 Å),

TABLE 1. Coordinates of Nonhydrogen Atoms (×10⁴) and of Hydrogen Atoms (×10³) of the Molecule of Compound III

Atom	x/a (σ)	y/b (σ)	z/c (σ)	Atom	x/a (σ)	y/b (σ)	z/c (σ)
O	5008(2)	−719(3)	3928(2)	$C_{(20)}$	3640(2)	2966(4)	495(3)
$N_{(1)}$	2771(2)	1685(3)	3279(3)	$C_{(21)}$	4149(2)	2288(4)	938(3)
$N_{(2)}$	3884(2)	996(3)	4446(2)	$C_{(22)}$	4076(2)	1820(4)	1763(3)
$C_{(1)}$	3242(2)	909(4)	4720(3)	$H_{(2)}$	356(2)	37(3)	600(3)
$C_{(2)}$	3140(2)	567(4)	5561(3)	$H_{(3)}$	240(2)	30(4)	638(3)
$C_{(3)}$	2486(3)	571(4)	5803(3)	$H_{(4)}$	145(2)	90(3)	539(3)
$C_{(4)}$	1926(2)	925(4)	5224(3)	$H_{(5)}$	163(2)	156(3)	397(2)
$C_{(5)}$	2026(2)	1263(4)	4382(3)	$H_{(8)}$	441(2)	115(3)	337(2)
$C_{(6)}$	2682(2)	1251(4)	4121(3)	$H_{(9.1)}$	343(2)	−95(3)	344(3)
$C_{(7)}$	3362(2)	1530(4)	3007(3)	$H_{(9.2)}$	383(2)	−58(3)	260(2)
$C_{(8)}$	3936(2)	812(4)	3516(3)	$H_{(12)}$	542(2)	−278(3)	425(3)
$C_{(9)}$	3867(2)	−506(4)	3243(3)	$H_{(13)}$	534(2)	−491(3)	421(3)
$C_{(10)}$	4500(2)	−1239(4)	3588(3)	$H_{(14)}$	451(2)	−592(4)	334(3)
$C_{(11)}$	4483(2)	−2556(4)	3488(3)	$H_{(15)}$	356(2)	−482(4)	257(3)
$C_{(12)}$	5019(2)	−3220(4)	3930(3)	$H_{(16)}$	355(2)	−272(3)	270(2)
$C_{(13)}$	5023(2)	−4447(4)	3865(3)	$H_{(18)}$	252(2)	288(3)	191(2)
$C_{(14)}$	4480(3)	−5030(4)	3374(3)	$H_{(19)}$	269(2)	365(3)	58(3)
$C_{(15)}$	3947(3)	−4387(4)	2935(3)	$H_{(20)}$	368(2)	331(4)	−9(3)
$C_{(16)}$	3944(2)	−3150(4)	2995(3)	$H_{(21)}$	462(2)	215(4)	70(3)
$C_{(17)}$	3472(2)	2037(4)	2135(3)	$H_{(22)}$	449(2)	133(4)	209(3)
$C_{(18)}$	2963(2)	2721(4)	1673(3)	H(N)	424(2)	79(3)	478(2)
$C_{(19)}$	3041(2)	3180(4)	860(3)				

TABLE 2. Some Valence Angles, ω°, of the Molecule of Compound III

Angle	ω	Angle	ω	Angle	ω
$C_{(6)}C_{(1)}N_{(2)}$	117,0(3)	$C_{(4)}C_{(5)}C_{(6)}$	120,4(3)	$C_{(8)}C_{(7)}C_{(17)}$	118,8(3)
$C_{(1)}N_{(2)}C_{(8)}$	117,7(3)	$C_{(5)}C_{(6)}C_{(1)}$	119,6(3)	$C_{(8)}C_{(9)}C_{(10)}$	112,4(3)
$N_{(2)}C_{(8)}C_{(7)}$	107,1(3)	$C_{(1)}N_{(2)}H(N)$	121(2)	$C_{(8)}C_{(9)}H_{(9.1)}$	115(2)
$C_{(8)}C_{(7)}N_{(1)}$	122,9(3)	$C_{(8)}N_{(2)}H(N)$	114(2)	$C_{(8)}C_{(9)}H_{(9.2)}$	110(2)
$C_{(7)}N_{(1)}C_{(6)}$	117,8(3)	$N_{(2)}C_{(8)}C_{(9)}$	112,9(3)	$C_{(10)}C_{(9)}H_{(9.1)}$	107(2)
$N_{(1)}C_{(6)}C_{(1)}$	121,5(3)	$C_{(7)}C_{(8)}C_{(9)}$	109,4(3)	$C_{(10)}C_{(9)}H_{(9.2)}$	105(2)
$C_{(6)}C_{(1)}C_{(2)}$	119,9(3)	$N_{(2)}C_{(8)}H_{(8)}$	109(2)	$H_{(9.1)}C_{(9)}H_{(9.2)}$	107(3)
$C_{(1)}C_{(2)}C_{(3)}$	119,7(4)	$C_{(7)}C_{(8)}H_{(8)}$	109(2)	$C_{(9)}C_{(10)}C_{(11)}$	119,4(3)
$C_{(2)}C_{(3)}C_{(4)}$	121,3(4)	$C_{(9)}C_{(8)}H_{(8)}$	109(2)	$C_{(9)}C_{(10)}O$	118,9(3)
$C_{(3)}C_{(4)}C_{(5)}$	119,2(4)	$N_{(1)}C_{(7)}C_{(17)}$	118,2(3)	$C_{(11)}C_{(10)}O$	121,7(3)

while the $C_{(8)}$ atom is removed even by 0.56 Å (in the same direction as the $C_{(7)}$ atom). The $H_{(8)}$ atom occupies a pseudoequatorial position, and the phenacyl substituent a pseudoaxial position. In the existing conformation a p-orbital orientation of the $N_{(2)}$ atom is realized also which is favorable for conjugation with the π-electronic system.

Inclusion in a six-membered heterocycle leads to fixation and considerable compression of the main chromophore grouping $N{-}C_{(6)}H_{(4)}{-}N{=}C{-}C_{(6)}H_{(5)}$. Thus, the $C_{(1)}{-}C_{(6)}{-}N_{(1)}{=}C_{(7)}$ torsion angle is 14.0° (Table 3), which is much less than in the aromatic derivatives of 2,3-dihydro-1H-1,5-benzodiazepine (39.4° [8]). Also the plane of the 3-phenyl group is rotated by a small angle (5.5°) with respect to the bicyclic ring. The compression of the chromophore fragment of the molecules is reflected in their spectral properties. This is manifested in the noticeable bathochromic shift of the long-wave absorption band of the aromatic derivatives of 1,2-dihydroquinoxaline, compared with 2,3-dihydro-1H-1,5-benzodiazepines containing the same chromophore group, and in the occurrence of luminescent properties in dihydroquinoxalines [6, 9]. It is interesting to note that the annelation of dihydroquinoxalines by the azirine ring causes an opposite effect, which is probably due to the p-orbital of the $N_{(1)}$ atom in azirinoquinoxalines having an orientation unfavorable for conjugation [10].

The reason for the formation of 1,2-dihydroquinoxalines [2-4] is the high thermodynamic favorability for the formation of a six-membered heterocyclic ring, compared with the seven-membered one. In this case, the data of [11], in which, without any convincing proof, a diazepine structure V was ascribed to the product of the reaction of ditoluylethylene with 1,3-dimethyl-5,6-diaminouracil, appear to be paradoxical. This prompted us to carry out a repeat investigation. We examined two possible structures of the compound studied: the di-

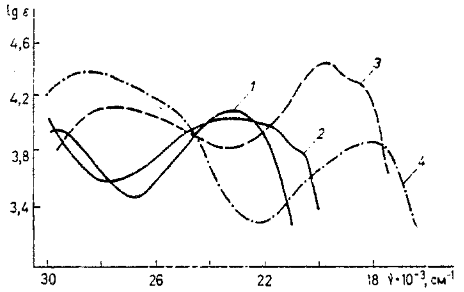
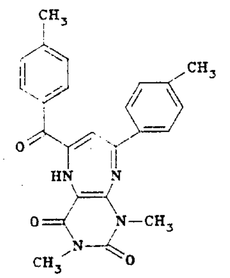


Fig. 2. UV spectra: 1) of compound VI in methanol; 2) of compound VII in methanol; 3) of compound VI in CF_3COOH; 4) of compound VII in CF_3COOH.

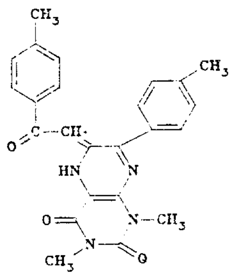
TABLE 3. Some Torsion Angles, τ°, of Molecule of Compound III

Angle	τ	Angle	τ	Angle	τ
$N_{(1)}C_{(6)}C_{(1)}N_{(2)}$	−1,0(2)	$C_{(8)}C_{(7)}N_{(1)}C_{(6)}$	5,6(3)	$C_{(6)}N_{(1)}C_{(7)}C_{(17)}$	−177,1(3)
$C_{(6)}C_{(1)}N_{(2)}C_{(8)}$	−30,5(3)	$C_{(7)}N_{(1)}C_{(6)}C_{(1)}$	14,0(3)	$N_{(2)}C_{(8)}C_{(7)}C_{(17)}$	149,0(3)
$C_{(1)}N_{(2)}C_{(8)}C_{(7)}$	45,9(3)	$N_{(1)}C_{(7)}C_{(17)}C_{(22)}$	−174,5(3)	$C_{(8)}C_{(7)}C_{(17)}C_{(22)}$	2,9(3)
$N_{(2)}C_{(8)}C_{(7)}N_{(1)}$	−33,8(3)				

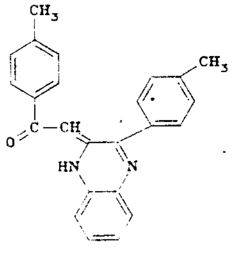
azepine V and the quinoxaline structure VI. The only proof for structure V given in [11] is the substantial deepening in the color on transition from alcoholic solutions of this compound to its solutions in trifluoroacetic acid. This corresponds to an intensely colored diazatropylium cation [11]:



V



VI



VII

We synthesized the compound with mp 253-255°C according to [11]. The analytical and spectral characteristics of the compound obtained coincided with the data in [11], and, except for the electronic spectra, equally corresponded to structures V and VI under consideration. To facilitate the interpretation of the spectral data for a model compound, by boiling a solution of ditoluylethylene and o-phenylenediamine in acetic acid [5], we synthesized 2-(4-methylphenacylidene)-3-(4-tolyl)-1,2-dihydroquinoxaline (VII), a homolog of compound IV. The identity of the preparation conditions of compounds IV and VII, as well as the similarity in their spectral characteristics (see [5] and the experimental part), provide evidence of the structure of VII.

The electronic absorption spectra of the compounds synthesized, measured in methanol and trifluoroacetic acid, are listed in Fig. 2. Here it must be noted that the spectra of the two compounds, measured in methanol containing HCl or CF_3COOH in a concentration of 2-3 moles/liter practically did not differ from the spectra of the neutral solutions. This alone refutes the structure V for the compound studied, since under these conditions, the diazepine derivatives convert into a protonated deeply colored aromatic form [12]. The spectra of compounds VI and VII in CF_3COOH, as in methanol, are similar (see Fig. 2). The appearance of a long-wave band with λ_{max} 548 nm takes place also in the model compound VII, and hence there are no reasons to consider the 1,5-diazepine structure of the product of the condensation of ditoluylethylene with 1,3-dimethyl-5,6-diaminouracil. Thus the structure of 5,7-dimethyl-6,8-dioxo-2-(4-methylphenacylidene)-3-(4-tolyl)-1,2-dihydropyrimidino[5,6-b]pyrazine (VI) should be ascribed to this compound.

EXPERIMENTAL

X-Ray Diffraction Analysis. Crystals of 2-phenacyl-3-phenyl-1,2-dihydroquinoxaline $C_{22}H_{18}N_2O$; at 20°C a = 19.624(2), b = 11.1915(7), c = 15.369(1) Å, β = 96.981(6)°, Z = 8,

$d_{\text{calc}} = 1.290$ g/cm^3, space group C2/c. The cell parameters and the intensity of 1388 independent reflections with $|F| \geq 2\sigma$ were measured on an automatic 4-circle Hilger-Watts diffractometer ($\lambda_{\text{CuK}_\alpha}$).

The structure was interpreted directly using the MULTAN program. All the hydrogen atoms were revealed objectively in a differential synthesis. The refinement in an anisotropic (isotropic for hydrogen atoms) approximation was carried up to $R = 0.048$ ($R_w = 0.038$). The atom coordinates, certain valence and torsion angles are listed in Tables 1-3.

The IR spectra of compounds VI and VII were measured in CCl_4 solutions ($c = 10^{-3}$ mole/liter) on a Specord IR-75 spectrophotometer, the electronic absorption spectra in methanol and trifluoroacetic acid [$c = (3\text{-}4)\cdot10^{-5}$ mole/liter] on a Specord UV-vis spectrometer, the PMR spectra in CF_3COOH solutions on a Varian XL-100 spectrometer, using TMS an internal standard. The individual state of the compounds was monitored by TLC on Silufol UV-254 plates, with chloroform as eluent.

The methods of preparation and purification of compounds III and VI were described previously: III in [5, 6], VI in [11].

2-(4-Methylphenacylidene)-3-(4-tolyl)-1,2-dihydroquinoxaline (VII) was obtained from o-phenylenediamine and ditroluylethylene [5] for compound IV. Orange crystals, mp 172°C. Yield 50%. IR spectrum: $\nu_{C=N}$ 1608, $\nu_{C=O}$ 1680 cm^{-1}. UV spectrum (in methanol) $\lambda_{\max}$ ($\varepsilon\cdot10^{-3}$): 241 (35.0), 329 (15.6), 435 nm (11.9). PMR spectrum: 1.99 (3H, s, CH_3); 2.11 (3H, s, CH_3); 6.35 (1H, s, CH), 6.77-8.15 ppm (12H, m, ArH). Found, %: N 7.9. $C_{24}H_{20}N_2O$. Calculated, %: N 8.0.

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