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REACTION OF 4-NITRO-1,2-PHENYLENEDIAMINE WITH 1-(4-R-PHENYL)-3-(4-NITROPHENYL)PROPENONES

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By the reaction of 4-nitro-1,2-phenylenediamine with 1-(p-R-phenyl)-3-(4-nitrophenyl)propenones, Michael adducts with a 1:2 composition have been obtained. A stagewise scheme is proposed for the formation of these compounds. The structure of one of the products has been established by means of x-ray structure analysis.

Continuing our studies of the reactivity of nitrogen-containing 1,4-dinucleophiles, we have investigated the reaction of 4-nitro-1,2-phenylenediamine (I) with 4-nitrochalcones (IIa-f). It is known [1] that 1,2-phenylenediamine derivatives containing electron-acceptor groups exhibit low reactivity in relation to chalcones. In contrast, 1,2-phenylenediamines with electron-donor substituents, in reactions with α,β-unsaturated ketones, readily form derivatives of 1,5-benzodiazepine [2].

We have shown that interaction of the diamine I with the chalcones IIa-f leads to the formation of the adducts IIIa-f (Table 1). The optimal conditions for synthesis of the diazepines IIIa-f are as follows: methanol solvent, reaction mixture refluxed for 12-20 h, diamine I in excess over chalcone IIa-f, catalyst 8-10 drops of acetic or hydrochloric acid. The use of acetic acid is preferred; in a number of experiments with added hydrochloric acid, the main product proved to be 5-(6)-nitro-2-(4-nitrophenyl)benzimidazole (IV), identified by comparison with the known product described in [3]. Recovery of compound IV is evidence in favor of the intermediate III′, which undergoes an acid-catalyzed benzimidazole rearrangement, the direction

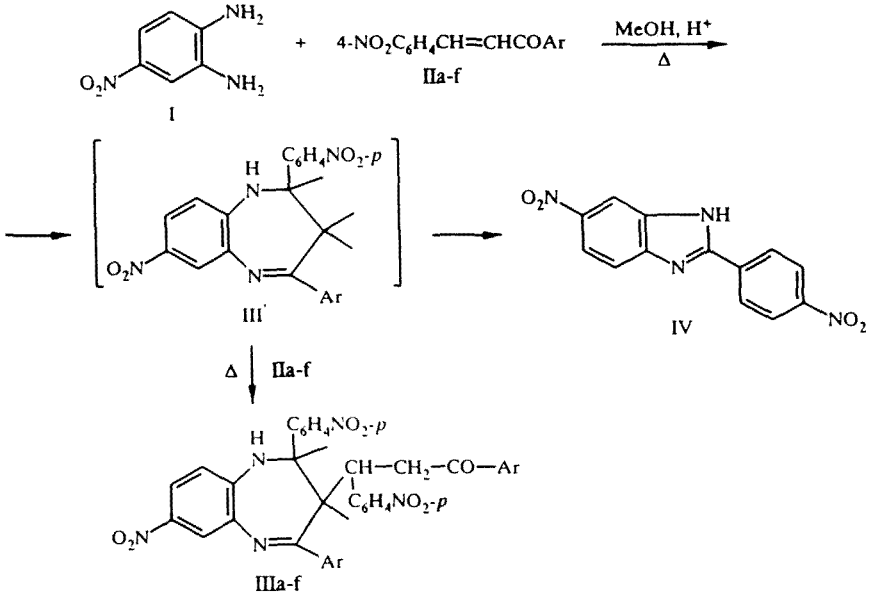

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TABLE 1. Characteristics of Synthesized Compounds IIIa-f and VIf-h

Compound	mp, °C	Found, %, N	Empirical formula	Calculated, %, N	UV spectrum, λ_{max} (and $\varepsilon \cdot 10^{-3}$)	IR spectrum, cm^{-1}				Yield, %
						$\nu_{NO_2}^{s}$	$\nu_{NO_2}^{as}$	$\nu_{C=O}$	ν_{NH}	
IIIa	205...206	10,6	$C_{36}H_{27}N_5O_7$	10,9	265 (45,3) 305 infl. 381 (19,0)	1302 1335 1348	1522 1529 1535	1655	3323	20
IIIb	240...241	10,4	$C_{38}H_{31}N_5O_7$	10,5	265 (50,2) 308 infl. 385 (18,1)	1320 1347	1513 1545	1668	3356	30
IIIc	204...205	9,8	$C_{40}H_{35}N_5O_7$	10,0	309 (50,4) 386 sh.	1315 1342	1515 1528	1662	3376	20
IIId	179...180	8,7	$C_{48}H_{35}N_5O_7$	8,8	315 (52,0) 386 sh.	1335 1328 1349	1519 1522	1662	3388	68
IIIe	217...218	14,3	$C_{36}H_{30}N_7O_7$	14,6	306 (56,2) 400 sh.	1315 1342	1515 1522	1642	3236* 3390 3473	35
IIIf	185...186	8,6	$C_{36}H_{25}Br_2N_5O_7$	8,8	317 (53,5) 387 sh.	1315 1340	1522	1662		38
VIf	19?...194	8,2	$C_{22}H_{17}Br_2N_3O_2$	8,1	271 (19,4) 384 (19,0)	1322	1522	1629†	3390	25
VIg	194...195	9,6	$C_{22}H_{17}Cl_2N_3O_2$	9,8	270 (19,7) 382 (20,1)	1315	1502	1625†	3390	40
VIh	228	15,3	$C_{22}H_{17}N_5O_6$	15,6	277 (24,2) 383 (17,8)	1325	1512	1628†	3369	62

*ν_{NH}, $\nu_{NH_2}^{s,as}$.

†ν_{C-N} in place of $\nu_{C=O}$.

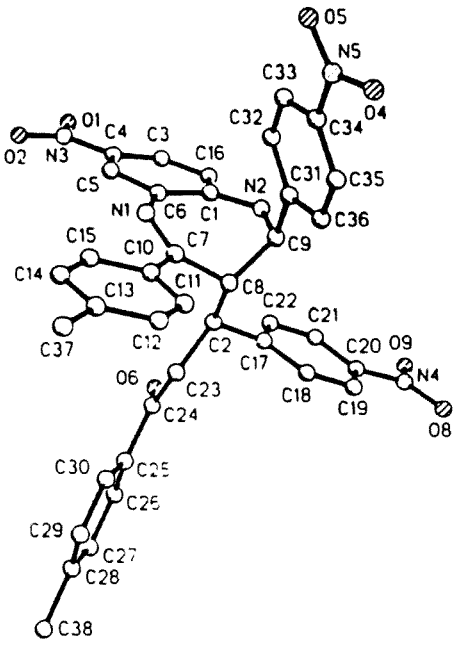


Fig. 1. Structure of compound IIIb.

of which is consistent with data reported in [4]. Basic catalysis (by triethylamine or sodium ethylate) or the use of triethylamine as the medium for the reaction between the diamine I and the chalcone IIa does not produce any products of interaction (as monitored by TLC).

The benzodiazepines IIIa-f were identified by means of IR and UV spectroscopy and in some cases by PMR spectroscopy; also, compound IIIb was subjected to x-ray structure analysis.

In the IR spectra (Table 1), we observe a complex spectral pattern in the region of symmetric (1312-1349 cm^{-1}) and asymmetric (1512-1548 cm^{-1}) vibrations of the nitro group; bands of stretching vibrations of the C=N bond are manifested (1602-1612 cm^{-1}), and also bands of $\nu_{C=O}$ at 1642-1668 cm^{-1}. Bands of ν_{NH} are found in the 3323-3388 cm^{-1} region; these bands are medium-intensity and are somewhat broadened.

For the diazepines IIIa-f, we observe two types of UV spectra. For compounds IIIa,b we observe a high-intensity band in the 265 nm region, a shoulder in the 305 nm region, and also intense long-wave absorption (see Table 1). In the adducts IIIc-f, the bands are redistributed: we observe an intense band in the 309-317 nm interval and an inflection in the region of 389-400 nm.

The PMR spectra of the diazepines IIIa,b,d, measured in DMSO-d_6, are in good agreement with the structure indicated above (see Experimental section).

The reduced nucleophilicity of the amino group of the diamine I, together with the high probability of the benzimidazole rearrangement, provides an explanation for the low yields of compounds IIIa-f. Stabilization of intermediates of the type of III′ is possible only as a result of their nucleophilic addition to the activated C=C bond of the ketones IIa-f. As indicated by the experimental data, the double bond of the α,β-unsaturated ketone is activated adequately only when a nitro group is present. Neither the chalcone or its 4-methyl, 4-methoxy, 4-chloro, 3-nitro, or 2-nitro derivatives will react with the diamine I. Also, the 4,4′-dinitrochalcone does not participate in any interaction.

It is known that the reactivity of CH-acids is determined by the ease of deprotonation, and that the reactivity increases as electron-acceptor groups are accumulated in the molecule [5]. The reactivity is significantly reduced in the case of 2-(p-nitrophenyl)-4-(p-methylphenyl)-2,3-dihydro-1H-1,5-benzodiazepine, which, in reaction with the chalcone IIb (refluxing equimolar quantities of the original components in methanol with catalytic quantities of hydrochloric acid), undergoes hydrolytic cleavage, forming o-phenylenediamine. Replacement of the nitro group by the C≡N group in the molecule of the diamine I also lowers the reactivity: 4-cyano-1,2-phenylenediamine in reactions with the chalcones IIa-f does not form any Michael adducts. Steric loading of a CH-acid, at the same time, favors the occurrence of an orbital-controlled process of nucleophilic addition; this can explain the satisfactory yields of compounds IIId,f.

TABLE 2. Coordinates of Nonhydrogen Atoms ($\times 10^4$) in Structure of IIIb

Atom	x	y	z	Atom	x	y	z
$N_{(1)}$	1680(4)	7115(3)	2755(3)	$C_{(17)}$	4280(5)	8076(3)	4807(4)
$N_{(2)}$	2636(5)	8591(3)	3181(3)	$C_{(18)}$	4087(6)	8301(4)	5502(4)
$N_{(3)}$	3727(6)	7068(4)	801(4)	$C_{(19)}$	4693(7)	8841(4)	5914(4)
$N_{(4)}$	6147(6)	9765(3)	6043(5)	$C_{(20)}$	5511(6)	9173(3)	5622(4)
$N_{(5)}$	-2929(6)	8864(4)	2717(5)	$C_{(21)}$	5710(6)	8970(4)	4924(4)
$O_{(1)}$	4398(7)	7322(4)	477(4)	$C_{(22)}$	5096(6)	8426(3)	4520(4)
$O_{(2)}$	3300(5)	6492(3)	629(3)	$C_{(23)}$	3740(6)	6816(3)	4790(4)
$O_{(4)}$	-3448(5)	9004(4)	3214(4)	$C_{(24)}$	4965(6)	6538(3)	4978(4)
$O_{(5)}$	-3426(5)	8849(4)	2024(4)	$C_{(25)}$	5283(6)	5942(3)	5532(4)
$O_{(6)}$	5673(4)	6788(3)	4685(3)	$C_{(26)}$	6422(6)	5777(4)	5831(4)
$O_{(8)}$	5934(6)	9958(3)	6656(4)	$C_{(27)}$	6767(7)	5236(4)	6356(5)
$O_{(9)}$	6848(6)	10048(3)	5776(4)	$C_{(28)}$	5941(7)	4841(4)	6565(4)
$C_{(1)}$	2884(5)	8169(3)	2630(4)	$C_{(29)}$	4797(6)	4994(4)	6249(4)
$C_{(2)}$	3685(5)	8430(4)	2254(4)	$C_{(30)}$	4457(6)	5530(4)	5723(4)
$C_{(3)}$	3974(6)	8071(4)	1659(4)	$C_{(31)}$	686(6)	8539(3)	3455(4)
$C_{(4)}$	3446(7)	7449(4)	1424(4)	$C_{(32)}$	129(6)	8606(4)	2672(4)
$C_{(5)}$	2653(6)	7176(4)	1794(4)	$C_{(33)}$	-1071(6)	8702(4)	2434(5)
$C_{(6)}$	2405(6)	7503(3)	2425(4)	$C_{(34)}$	-1673(6)	8744(4)	2985(5)
$C_{(7)}$	1592(5)	7157(3)	3472(4)	$C_{(35)}$	-1129(6)	8685(4)	3766(5)
$C_{(8)}$	2246(5)	7666(3)	4064(4)	$C_{(36)}$	72(6)	8575(4)	4009(4)
$C_{(9)}$	2000(6)	8419(3)	3748(4)	$C_{(37)}$	-1542(8)	5157(5)	4262(6)
$C_{(10)}$	819(6)	6657(3)	3703(4)	$C_{(38)}$	6300(7)	4251(4)	7150(5)
$C_{(11)}$	369(7)	6739(4)	4330(5)	$O_{(11)}$	1780(11)	8461(9)	6052(8)
$C_{(12)}$	-388(8)	6263(4)	4501(5)	$O_{(12)}$	1381(10)	8699(5)	7139(6)
$C_{(13)}$	-710(7)	5684(4)	4066(5)	$C_{(40)}$	1462(14)	8859(10)	6514(11)
$C_{(14)}$	-249(6)	5580(4)	3438(5)	$C_{(41)}$	808(15)	9430(8)	6094(9)
$C_{(15)}$	476(6)	6067(4)	3250(4)	$C_{(42)}$	1913(13)	8134(8)	7465(8)
$C_{(16)}$	3575(6)	7498(3)	4335(4)	$C_{(43)}$	1752(12)	7940(7)	8136(8)

The formation of Michael adducts in the reaction of 4,5-diamino-1,6-dihydropyrimidin-6-one with chalcones (mole ratio of original components 1:2) is reported in [6]. In our experiments, such a ratio of the diamine I and chalcones IIa-f hindered the interaction, and the corresponding diazepines IIIa-f were not recovered.

In order to determine the sequence of stages in forming the adducts IIIa-f, we used the diamine I and acetophenones Vf-h to obtain the benzodiazepines VIf-h, containing a methyl group in position 2 of the seven-membered ring (this group providing a substantial increase of stability of the compounds [7]). PMR data indicate that compounds VIf-h are the 7-nitro isomers, as evidenced by the position and multiplicity of signals of the 6H and 9H protons of the phenylene ring (see Experimental section). The acetophenones Va,b,e in their reactions with the diamine I form the corresponding monoazomethines VIIa,b,e. We consider that the formation of the diazepines VIf,h, which contain electron-acceptor groupings in the 4-aryl fragment, is related to manifestation of conjugation effects in the system that tend to increase the thermodynamic stability of the desired products.

We carried out the reaction of compounds VIf-h with the chalcone IIa in methanol in the presence of catalytic quantities of hydrochloric acid. As a result of prolonged refluxing, we still recovered only the original components from the reaction mixture.

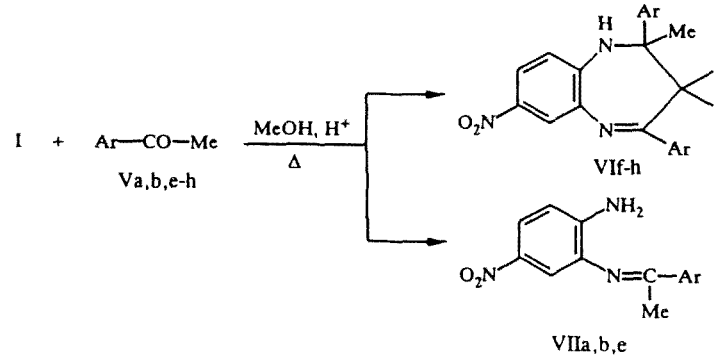
The question of the direction taken in the formation of the diazepine ring in compounds IIIa-f was answered unambiguously on the basis of x-ray structure analysis of compound IIIb (see below), according to which the more basic 2-amino group of the diamine I participates in the formation of the azomethine group. This result eliminates a possible interpretation of the process of diazepine ring formation as proceeding through a stage of β-addition, as had been observed in [8] for the reaction of the diamine I with 4-nitrochalcone dibromides under conditions of basic catalysis.

Consequently, under conditions of an acid-catalyzed process, the first stage in the reaction of the diamine I with the chalcones IIa-f is 1,2-addition through the carbonyl group of the α,β-unsaturated ketone.

According to the x-ray diffraction data, compound IIIb is a crystal solvate of the product obtained by the addition of 2-(p-nitrophenyl)-4-(p-methylphenyl)-7-nitro-2,3-dihydro-1H-1,5-benzodiazepine to 1-(p-methylphenyl)-3-(p-nitrophenyl)propenone, with one molecule of ethyl acetate (see Fig. 1 and Tables 2-5).

TABLE 3. Bond Lengths (Å) in Structure of IIIb

Bond	l	Bond	l
$N_{(1)}$—$C_{(6)}$	1,391(9)	$N_{(1)}$—$C_{(7)}$	1,302(9)
$N_{(2)}$—$H_{N(2)}$	1,23(4)	$N_{(2)}$—$C_{(1)}$	1,367(9)
$N_{(2)}$—$C_{(9)}$	1,452(9)	$N_{(3)}$—$O_{(1)}$	1,21(1)
$N_{(3)}$—$O_{(2)}$	1,23(1)	$N_{(3)}$—$C_{(4)}$	1,44(1)
$N_{(4)}$—$O_{(8)}$	1,24(1)	$N_{(4)}$—$O_{(9)}$	1,20(1)
$N_{(4)}$—$C_{(20)}$	1,466(9)	$N_{(5)}$—$O_{(4)}$	1,24(1)
$N_{(5)}$—$O_{(5)}$	1,21(1)	$N_{(5)}$—$C_{(34)}$	1,46(1)
$O_{(6)}$—$C_{(24)}$	1,21(1)	$C_{(1)}$—$C_{(6)}$	1,423(9)
$C_{(1)}$—$C_{(2)}$	1,40(1)	$C_{(16)}$—$C_{(8)}$	1,562(9)
$C_{(16)}$—$C_{(17)}$	1,511(9)	$C_{(16)}$—$C_{(23)}$	1,536(9)
$C_{(3)}$—$C_{(4)}$	1,38(1)	$C_{(3)}$—$C_{(2)}$	1,38(1)
$C_{(4)}$—$C_{(5)}$	1,39(1)	$C_{(5)}$—$C_{(6)}$	1,38(1)
$C_{(7)}$—$C_{(8)}$	1,498(8)	$C_{(7)}$—$C_{(10)}$	1,47(1)
$C_{(8)}$—$C_{(9)}$	1,567(9)	$C_{(9)}$—$C_{(31)}$	1,531(9)
$C_{(10)}$—$C_{(11)}$	1,37(1)	$C_{(10)}$—$C_{(15)}$	1,395(9)
$C_{(11)}$—$C_{(12)}$	1,38(1)	$C_{(12)}$—$C_{(13)}$	1,36(1)
$C_{(13)}$—$C_{(14)}$	1,38(1)	$C_{(13)}$—$C_{(37)}$	1,53(1)
$C_{(14)}$—$C_{(15)}$	1,38(1)	$C_{(17)}$—$C_{(18)}$	1,38(1)
$C_{(17)}$—$C_{(22)}$	1,39(1)	$C_{(18)}$—$C_{(19)}$	1,37(1)
$C_{(19)}$—$C_{(20)}$	1,38(1)	$C_{(20)}$—$C_{(21)}$	1,38(1)
$C_{(21)}$—$C_{(22)}$	1,373(9)	$C_{(23)}$—$C_{(24)}$	1,510(9)
$C_{(24)}$—$C_{(25)}$	1,497(9)	$C_{(25)}$—$C_{(26)}$	1,36(1)
$C_{(25)}$—$C_{(30)}$	1,38(1)	$C_{(26)}$—$C_{(27)}$	1,39(1)
$C_{(27)}$—$C_{(28)}$	1,38(1)	$C_{(28)}$—$C_{(29)}$	1,36(1)
$C_{(28)}$—$C_{(38)}$	1,53(1)	$C_{(29)}$—$C_{(30)}$	1,38(1)
$C_{(31)}$—$C_{(32)}$	1,368(9)	$C_{(31)}$—$C_{(36)}$	1,38(1)
$C_{(32)}$—$C_{(33)}$	1,39(1)	$C_{(33)}$—$C_{(34)}$	1,36(1)
$C_{(34)}$—$C_{(35)}$	1,36(1)	$C_{(35)}$—$C_{(36)}$	1,40(1)
$O_{(11)}$—$C_{(40)}$	1,26(3)	$O_{(12)}$—$C_{(40)}$	1,18(2)
$O_{(12)}$—$C_{(42)}$	1,32(2)	$C_{(40)}$—$C_{(41)}$	1,44(2)
$C_{(42)}$—$C_{(43)}$	1,31(2)		



II-VII: a-h)Ar = C_6H_4R-*p*; a)R = H, b)R = Me, c)R = Et, d)R = Ph, e)R = NH_2, f)R = Br, g)R = Cl, h)R = NO_2

The diazepine ring exists in the twist-boat conformation. The $N_{(1)}$, $N_{(2)}$, $C_{(1)}$, $C_{(6)}$, and $C_{(9)}$ atoms lie in a single plane with an accuracy of 0.03 Å; the $C_{(7)}$ and $C_{(8)}$ deviate from this plane by 0.45(1) and 1.04(1) Å, respectively.

Substituents on the $C_{(8)}$ and $C_{(9)}$ atoms occupy axial and pseudoaxial positions, respectively (torsion angles $N_{(1)}-C_{(7)}-C_{(8)}-C_{(16)}$ −70.0(7)°, $C_{(1)}-N_{(2)}-C_{(9)}-C_{(31)}$ −89.9(7)°). The nitrophenyl group at $C_{(9)}$ is turned very nearly parallel to the $N_{(2)}-C_{(9)}$ bond (torsion angle $N_{(2)}-C_{(9)}-C_{(31)}-C_{(32)}$ 18.0(8)°), apparently because of nonvalence interactions between the atoms $H_{(8)}/H_{(36)}$, $H_{(8)}/C_{(36)}$, and $N_{(2)}/H_{(32)}$, the distances between which — 2.28(1), 2.71(1), and 2.54(1) Å, respectively — are smaller than the sums of the van der Waals radii (2.32, 2.87, and 2.66 Å, respectively).

TABLE 4. Bond Angles (deg) in Structure of IIIb

Bond angles	ω	Bond angles	ω
$C_{(6)}-N_{(1)}-C_{(7)}$	126,9(5)	$H_{N(2)}-N_{(2)}-C_{(1)}$	112,6(21)
$H_{N(2)}-N_{(2)}-C_{(9)}$	116,6(21)	$C_{(1)}-N_{(2)}-C_{(9)}$	127,6(5)
$C_{(1)}-N_{(3)}-O_{(2)}$	122,5(8)	$O_{(1)}-N_{(3)}-C_{(4)}$	118,3(7)
$O_{(2)}-N_{(3)}-C_{(4)}$	119,2(7)	$O_{(8)}-N_{(4)}-O_{(9)}$	122,5(7)
$O_{(8)}-N_{(4)}-C_{(20)}$	118,7(7)	$O_{(9)}-N_{(4)}-C_{(20)}$	118,7(8)
$O_{(4)}-N_{(5)}-O_{(5)}$	121,5(7)	$O_{(4)}-N_{(5)}-C_{(34)}$	118,3(7)
$O_{(5)}-N_{(5)}-C_{(34)}$	120,1(9)	$N_{(2)}-C_{(1)}-C_{(6)}$	125,3(6)
$N_{(2)}-C_{(1)}-C_{(2)}$	115,4(6)	$C_{(6)}-C_{(1)}-C_{(2)}$	119,2(6)
$C_{(8)}-C_{(16)}-C_{(17)}$	112,4(5)	$C_{(8)}-C_{(16)}-C_{(23)}$	108,4(6)
$C_{(17)}-C_{(16)}-C_{(23)}$	112,4(5)	$C_{(4)}-C_{(3)}-C_{(2)}$	119,0(7)
$N_{(3)}-C_{(4)}-C_{(3)}$	120,0(7)	$N_{(3)}-C_{(4)}-C_{(5)}$	119,5(6)
$C_{(3)}-C_{(4)}-C_{(5)}$	120,5(7)	$C_{(4)}-C_{(5)}-C_{(6)}$	121,6(6)
$N_{(1)}-C_{(6)}-C_{(1)}$	129,7(6)	$N_{(1)}-C_{(6)}-C_{(5)}$	112,6(6)
$C_{(1)}-C_{(6)}-C_{(5)}$	117,7(6)	$N_{(1)}-C_{(7)}-C_{(8)}$	123,8(6)
$N_{(1)}-C_{(7)}-C_{(10)}$	116,8(5)	$C_{(8)}-C_{(7)}-C_{(10)}$	119,3(6)
$C_{(16)}-C_{(8)}-C_{(7)}$	111,7(5)	$C_{(16)}-C_{(8)}-C_{(9)}$	112,4(5)
$C_{(7)}-C_{(8)}-C_{(9)}$	110,9(5)	$N_{(2)}-C_{(9)}-C_{(8)}$	112,2(5)
$N_{(2)}-C_{(9)}-C_{(31)}$	114,4(5)	$C_{(8)}-C_{(9)}-C_{(31)}$	109,8(5)
$C_{(7)}-C_{(10)}-C_{(11)}$	124,3(6)	$C_{(7)}-C_{(10)}-C_{(15)}$	119,4(6)
$C_{(11)}-C_{(10)}-C_{(15)}$	116,3(7)	$C_{(10)}-C_{(11)}-C_{(12)}$	121,7(7)
$C_{(11)}-C_{(12)}-C_{(13)}$	122,1(9)	$C_{(12)}-C_{(13)}-C_{(14)}$	117,6(8)
$C_{(12)}-C_{(13)}-C_{(37)}$	121,8(9)	$C_{(14)}-C_{(13)}-C_{(37)}$	120,6(7)
$C_{(13)}-C_{(14)}-C_{(15)}$	120,3(7)	$C_{(10)}-C_{(15)}-C_{(14)}$	122,0(7)
$C_{(1)}-C_{(2)}-C_{(3)}$	121,5(6)	$C_{(16)}-C_{(17)}-C_{(18)}$	121,6(6)
$C_{(2)}-C_{(17)}-C_{(22)}$	120,1(6)	$C_{(18)}-C_{(17)}-C_{(22)}$	118,2(6)
$C_{(17)}-C_{(18)}-C_{(19)}$	121,6(7)	$C_{(18)}-C_{(19)}-C_{(20)}$	119,1(7)
$N_{(4)}-C_{(20)}-C_{(19)}$	119,9(7)	$N_{(4)}-C_{(20)}-C_{(21)}$	119,2(7)
$C_{(19)}-C_{(20)}-C_{(21)}$	120,8(6)	$C_{(20)}-C_{(21)}-C_{(22)}$	119,2(7)
$C_{(17)}-C_{(22)}-C_{(21)}$	121,0(7)	$C_{(2)}-C_{(23)}-C_{(24)}$	113,8(6)
$O_{(6)}-C_{(24)}-C_{(23)}$	120,7(6)	$O_{(6)}-C_{(24)}-C_{(25)}$	120,7(6)
$C_{(23)}-C_{(24)}-C_{(25)}$	118,6(6)	$C_{(24)}-C_{(25)}-C_{(26)}$	119,1(6)
$C_{(24)}-C_{(25)}-C_{(30)}$	122,5(6)	$C_{(26)}-C_{(25)}-C_{(30)}$	118,3(6)
$C_{(25)}-C_{(26)}-C_{(27)}$	121,5(7)	$C_{(26)}-C_{(27)}-C_{(28)}$	119,9(7)
$C_{(27)}-C_{(28)}-C_{(29)}$	118,7(6)	$C_{(27)}-C_{(28)}-C_{(38)}$	120,8(7)
$C_{(29)}-C_{(28)}-C_{(38)}$	120,5(7)	$C_{(28)}-C_{(29)}-C_{(30)}$	121,3(7)
$C_{(25)}-C_{(30)}-C_{(29)}$	120,2(6)	$C_{(9)}-C_{(31)}-C_{(32)}$	121,9(7)
$C_{(9)}-C_{(31)}-C_{(36)}$	117,5(6)	$C_{(32)}-C_{(31)}-C_{(36)}$	120,5(6)
$C_{(31)}-C_{(32)}-C_{(33)}$	119,7(7)	$C_{(32)}-C_{(33)}-C_{(34)}$	119,6(7)
$N_{(5)}-C_{(34)}-C_{(33)}$	118,3(7)	$N_{(5)}-C_{(34)}-C_{(35)}$	120,3(8)
$C_{(33)}-C_{(34)}-C_{(35)}$	121,4(7)	$C_{(34)}-C_{(35)}-C_{(36)}$	119,4(8)
$C_{(31)}-C_{(36)}-C_{(35)}$	119,4(6)	$C_{(40)}-O_{(12)}-C_{(42)}$	118,6(15)
$O_{(11)}-C_{(40)}-O_{(12)}$	124,3(18)	$O_{(11)}-C_{(40)}-C_{(41)}$	110,9(16)
$O_{(12)}-C_{(40)}-C_{(41)}$	121,1(18)	$O_{(12)}-C_{(42)}-C_{(43)}$	117,7(15)

TABLE 5. Shortened Intermolecular Contacts in Crystal of Compound IIIb

Contact	Symmetry elements	Distance between atoms, Å	Sum of van der Waals radii, Å
$H_{(372)}...H_{(29)'}$	$-x, 1-y, 1-z$	2,23(1)	2,32
$H_{(373)}...C_{(13)'}$	$-x, 1-y, 1-z$	2,72(1)	2,87
$C_{(20)}...H_{(5)'}$	$0,5+x, 1,5-y, 0,5+z$	2,80(1)	2,87

In the substituent at the $C_{(8)}$ atom, the benzoyl and nitrophenyl groups are positioned in the synclinal conformation with respect to the $C_{(16)}-C_{(23)}$ bond (torsion angle $C_{(17)}-C_{(16)}-C_{(23)}-C_{(24)}$ $-64.1(8)°$). In turn, the $C_{(16)}-C_{(23)}$ bond is oriented synperiplanar with respect to the carbonyl group (dihedral angle $C_{(16)}-C_{(23)}-C_{(24)}-O_{(6)}$ $-10.5(9)°$). This group and the connected tolyl group lie in the same plane, to within 0.05 Å.

The system of the benzodiazepine ring is nonplanar (dihedral angles $C_{(1)}-C_{(6)}-N_{(1)}-C_{(7)}$ $-26.1(1)°$, $N_{(1)}-C_{(7)}-C_{(10)}-C_{(15)}$ $17.1(8)°$).

The rotation of the aromatic ring at the $C_{(7)}$ atom around the $C_{(7)}-C_{(10)}$ bond is probably due to nonvalence interactions between the atoms $H_{(8)}...H_{(11)}$ and $H_{(8)}...C_{(11)}$, the distances between which (1.98(1) and 2.61(1) Å) are substantially shorter than the sums of the van der Walls radii (2.32 and 2.87 Å, respectively). The nitro groups are practically coplanar with the planes of the benzene rings (torsion angle $C_{(5)}-C_{(4)}-N_{(3)}-O_{(2)}$ −3(1)°, $C_{(33)}-C_{(34)}-N_{(5)}-O_{(5)}$ 8(1)°).

In crystals, the molecules form centrosymmetric dimers as a result of intermolecular hydrogen bonding between the atom $H_{N(2)}$ and an oxygen atom of one of the nitro groups (distance $H_{N(2)}...O_{(8)}$ 2.07(1) Å, angle $N_{(2)}-N_{N(2)}...O_{(8)}$ 164.1(8)°). Shortened intermolecular contacts are also observed, as shown in Table 5.

EXPERIMENTAL

IR spectra were taken on an IR-75 spectrometer in KBr tablets; electronic absorption spectra were taken on a Specord UV-Vis instrument in methanol at a sample concentration of $1.5 \cdot 10^{-5}$ M; PMR spectra were taken on a Varian VXR-200 Gemini instrument in DMSO-d_6, internal standard TMS.

Elemental analyses of the synthesized compounds for nitrogen matched the calculated values.

X-Ray Structure Investigation of Compound IIIb. Crystals are monoclinic. At 20°C, a = 11.947(6), b = 19.445(5), c = 17.673(4) Å, β = 105.79(2)°, V = 3951(4) Å^3, d_{calc} = 1.264 g/cm^3, Z = 4, space group $P2_1/n$. The elementary cell constants and the intensities of 2378 reflections with $F > 6\sigma(F)$ were measured in an automatic four-circle Siemens P3/PC diffractometer on (MoKα radiation, graphite monochromator, $\theta/2\theta$ scanning, $2\theta_{max}$ = 50°).

The structure was deciphered by the direct method, using the program set SHELXTL PLUS. The positions of the hydrogen atoms were determined from a difference synthesis of electron density, without any subsequent refinement. For the nonhydrogen atoms, refinement by the block-diagonal least squares method in the anisotropic approximation was carried to R = 0.095 (R_w = 0.097, S = 2.64).

7-Nitro-2-(p-nitrophenyl)-4-phenyl-3-[β-(p-nitrophenyl)phenylpropanone-1]-2,3-dihydro-1H-1,5-benzodiazepine (IIIa). A mixture of 0.51 g (2.00 mmoles) of the chalcone IIa and 0.42 g (2.76 mmoles) of the diamine I in 50 ml of methanol, with the addition of 10 drops of acetic acid, was refluxed for 12 h. The solution was cooled, the unreacted diamine I and chalcone IIa were filtered off, and the filtrate was evaporated down to 3/4 original volume. The precipitated crystals of IIIa were recrystallized from ethyl acetate.

Compounds IIIb-g were synthesized analogously, with various times of refluxing the reaction mixture.

PMR spectra (DMSO-d_6), ppm: IIIa: 3.02 (1H, d, 3-CH), 3.27 (2H, s, CH_2), 3.42-3.52 (1H, dd, β-CH), 4.40 (1H, s. br., NH), 4.45 (1H, s, 2-H), 7.00-8.30 (21H, m. arom, CH). IIIb: 2.25 (3H, s, $-N{=}C-C_6H_4CH_3$), 2.49 (3H, s, $COC_6H_4CH_3$), 3.01 (1H, d, 3-CH), 3.27 (2H, s, CH_2), 3.46-3.55 (1H, dd, β-CH), 4.41 (1H, s. br., NH), 4.48 (1H, t, 2-H), 7.00-8.30 (19H, m. arom, CH). IIId: 3.21 (1H, d, 3-H), 3.28 (2H, s, CH_2), 3.67-3.79 (1H, dd, β-CH), 4.59 (1H, s. br., NH), 5.47 (1H, t, 2-H), 7.03-8.30 (29H, m. arom, CH).

7-Nitro-2-methyl-2,4-di-(p-bromophenyl)-2,3-dihydro-1H-1,5-benzodiazepine (VIf). A mixture of 2.08 g (10.45 mmoles) of the acetophenone Vf, 0.8 g (5.23 mmoles) of the diamine I, and eight drops of hydrochloric acid in 80 ml of methanol was refluxed for 10 h. Upon cooling, obtained 0.8 g (33%) of the diazepine VIf (from methanol).

The diazepines VIg,h were obtained analogously. PMR spectra (DMSO-d_6): VIf: 1.78 (3H, s, CH_3), 2.91 (1H, d, H_A, CH_2), 3.94 (1H, d, H_B, CH_2), 7.13 (1H, d, 9-H), 7.18-7.71 (8H, m), 7.78 (1H, s, NH), 7.89 (1H, q, 8-H), 8.02 (1H, d, 6-H). VIh: 1.83 (3H, s, CH_3), 3.05 (1H, d, H_A, CH_2), 4.25 (1H, d, H_B, CH_2), 7.22 (1H, q, 9-H), 7.25-7.82 (8H, m), 7.90 (1H, s, NH), 8.03 (1H, q, 8-H), 8.18. (1H, d, 6-H).

The azomethines VIIa,b,e were obtained by the procedure given above. **Compound VIIa ($C_{14}H_{13}N_3O_2$),** yield 47%, mp 239-240°C. UV spectrum (isopropanol): λ_{max} = 406 nm, $\varepsilon \cdot 10^{-3}$ = 19.3. IR spectrum (KBr), cm^{-1}: 1315, 1522, 1618, 3349, 3433. **Compound VIIb ($C_{15}H_{15}N_3O_2$),** yield 46%, mp 250-252°C. UV spectrum (isopropanol): λ_{max} = 408 nm, $\varepsilon \cdot 10^{-3}$ = 21.3. IR spectrum (KBr), cm^{-1}: 1322, 1529, 1622, 3363, 3443. **Compound VIIe ($C_{14}H_{14}N_4O_2$),** yield 43%, mp 283°C. UV spectrum (isopropanol): λ_{max} = 381 nm, $\varepsilon \cdot 10^{-3}$ = 28.0. IR spectrum (KBr), cm^{-1}: 1342, 1502, 1635, 3303, 3363, 3540. PMR spectrum (DMSO-d_6), ppm: 3.16 (3H, s, CH_3), 6.12 (2H, s. br., NH_2), aromatic protons: 6.82 (2H, d, J = 8.0 Hz), 7.83 (1H, d, J = 8.0 Hz), 8.10 (2H, d), 8.25 (1H, d), 8.42 (1H, s).

5-(6)-Nitro-2-(p-nitrophenyl)benzimidazole (IV). A mixture of 0.35 g (1.24 mmoles) of the chalcone IIb, 0.2 g (1.3 mmoles) of the diamine I, and six drops of hydrochloric acid in 40 ml of methanol was refluxed for 10 h. The solution was

evaporated down to 1/2 original volume; after cooling, compound IV was recovered (55%), mp 275°C. Literature value: mp 276-277°C [3].

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REFERENCES

1. N. N. Kolos, Candidate's Dissertation, Khar'kov (1982), p. 46.
2. B. O. Insuasty, R. G. Abonia, and J. P. Quiroga, An. Quim., **88**, No. 7-8, 718 (1994).
3. D. G. Bapat and N. V. Shirsat, Indian J. Chem., **3**, 81 (1965).
4. V. D. Orlov, N. N. Kolos, and B. M. Zolotarev, Khim. Geterotsikl. Soedin., No. 3, 390 (1983).
5. L. A. Yanovskaya, G. V. Kryshtal', and V. V. Kul'ganek, Usp. Khim., **53**, 1280 (1984).
6. B. O. Insuasty, M. Ramos, R. Moreno, and J. P. Quiroga, J. Heterocycl. Chem., in press.
7. V. D. Orlov and S. M. Desenko, Khim. Geterotsikl. Soedin., No. 12, 1673 (1985).
8. N. N. Kolos, V. D. Orlov, and E. Ya. Yuzefovskaya, Khim. Geterotsikl. Soedin., (1996), in press.