Synthesis and properties of 4,4′-substituted *O*-benzoylbenzamide oximes

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New *O*-benzoylbenzamide oximes have been synthesized and their u.v. and i.r. spectra are discussed.

Описывается синтез новых *O*-бензоилпроизводных бензамидоксимов и обсуждаются их УФ и ИК спектры.

As a part of the project involving the preparation, reactions, and properties of benzamide oximes, *O*-benzoylbenzamide oximes derivatives *I*—*XXVIII* (Scheme 1; Table 1) bearing at the position 4 in both rings substituents of markedly different polarity have been synthesized. Of the described series only compounds *I*, *III*—*VI* have so far been prepared and studied by i.r. spectroscopy [1—6]. The new substances *II*, *VII*—*XXVIII* were obtained by means of the Schotten—Baumann reaction in pyridine [7].

We have found that the electronic spectra of *O*-benzoylbenzamide oximes show one or two intense absorption bands at 230 and 270 nm. A pronounced bathochromic shift was observed with substances *VII*, *XIV*, *XXI*, and *XXVIII* bearing at the *p*-position (4) a $(CH_3)_2N$— group. The differences in molar absorption coefficients are small (Table 1).

Table 2 contains the wavenumbers for intense bands found in the i.r. spectra (measured in Nujol) of the prepared substances. In Table 3 are given the wavenumbers for the stretching vibration absorption bands of the NH_2 and $C=O$ groups (measured in carbon tetrachloride and acetonitrile), which correlate with the Hammett σ_p constants [8, 9]

$$\tilde{\nu} = \tilde{\nu}_0 + \varrho\sigma$$

Table 1

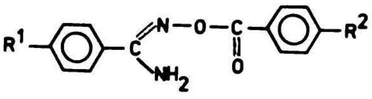
Characteristic of *O*-benzoylbenzamide oximes

Compound	R^1	R^2	Formula	*M*	Calculated/found			Yield	M.p.	λ, nm (log ε)
					% C	% H	% N	%	°C	
I	H	H								226 (4.24); 262 (4.03)
II	Cl	H	$C_{14}H_{11}ClN_2O_2$	274.69	61.21	4.04	10.20	84	163	231 (4.32); 266 (4.07)
					61.22	4.10	10.12			
III	Br	H								232 (4.34); 267 (4.12)
IV	CH_3	H								229 (4.28); 263 (4.06)
V	CH_3O	H								232 (4.23)
VI	NO_2	H								235 (4.24)
VII	$(CH_3)_2N$	H	$C_{16}H_{17}N_3O_2$	283.31	67.83	6.05	14.83	75	140	225 (4.27); 305 (4.29)
					67.99	6.19	14.63			
VIII	H	CH_3O	$C_{15}H_{14}N_2O_3$	270.27	66.66	5.22	10.36	69	146	269 (4.33)
					66.50	5.29	10.14			
IX	Cl	CH_3O	$C_{15}H_{13}ClN_2O_3$	304.72	59.12	4.30	9.9	62	170	272 (4.36)
					58.98	4.36	9.31			
X	Br	CH_3O	$C_{15}H_{13}BrN_2O_3$	349.17	51.59	3.75	8.02	61	173	235 (4.23); 273 (4.38)
					51.42	3.67	7.93			
XI	CH_3	CH_3O	$C_{16}H_{16}N_2O_3$	284.30	67.59	5.67	9.85	66	158	270 (4.37)
					67.63	5.74	9.56			
XII	CH_3O	CH_3O	$C_{16}H_{16}N_2O_4$	300.29	63.99	5.37	9.33	60	175	273 (4.38)
					63.98	5.44	9.29			
XIII	NO_2	CH_3O	$C_{15}H_{13}N_3O_5$	315.27	57.14	4.16	13.33	63	191	260 (4.41)
					57.01	4.18	13.15			
XIV	$(CH_3)_2N$	CH_3O	$C_{17}H_{19}N_3O_3$	313.34	65.16	6.11	13.41	58	161	259 (4.25); 310 (4.41)
					65.31	6.15	13.23			
XV	H	Cl	$C_{14}H_{11}ClN_2O_2$	274.69	61.21	4.04	10.20	86	178	240 (4.26)
					61.05	4.06	10.11			

Table 1 (Continued)

Compound	R^1	R^2	Formula	M	Calculated/found			Yield %	M.p. °C	λ nm (log ε)
					% C	% H	% N			
XVI	Cl	Cl	$C_{14}H_{10}Cl_2N_2O_2$	309.14	54.39 54.28	3.26 3.31	9.06 9.05	88	185	237 (4.31)
XVII	Br	Cl	$C_{14}H_{10}ClBrN_2O_2$	353.59	47.55 47.68	2.82 2.87	7.92 7.68	79	158	240 (4.36)
XVIII	CH_3	Cl	$C_{15}H_{13}ClN_2O_2$	288.72	62.40 62.16	4.54 4.51	9.70 9.50	86	176	240 (4.30)
XIX	CH_3O	Cl	$C_{15}H_{13}ClN_2O_3$	304.72	59.12 59.22	4.30 4.29	9.19 8.99	72	156	244 (4.33)
XX	NO_2	Cl	$C_{14}H_{10}ClN_3O_4$	319.69	52.59 52.82	3.15 3.20	13.14 13.18	87	184	246 (4.30)
XXI	$(CH_3)_2N$	Cl	$C_{16}H_{16}ClN_3O_2$	317.76	60.57 60.78	5.07 5.12	13.22 13.09	70	145	238 (4.26); 304 (4.33)
XXII	H	NO_2	$C_{14}H_{11}N_3O_4$	285.24	58.95 58.95	3.89 3.94	14.73 14.78	94	188	256 (4.23)
XXIII	Cl	NO_2	$C_{14}H_{10}ClN_3O_4$	319.69	52.59 52.58	3.15 3.14	13.14 13.19	92	175	257 (4.27)
XXIV	Br	NO_2	$C_{14}H_{10}BrN_3O_4$	364.14	46.17 46.10	2.77 2.86	11.54 11.57	92	184	250 (4.30)
XXV	CH_3	NO_2	$C_{15}H_{13}N_3O_4$	299.27	60.20 60.25	4.38 4.33	14.04 14.09	95	184	256 (4.27)
XXVI	CH_3O	NO_2	$C_{15}H_{13}N_3O_5$	315.27	57.14 57.08	4.16 4.06	13.33 13.34	87	178	256 (4.35)
XXVII	NO_2	NO_2	$C_{14}H_{10}N_4O_6$	330.24	50.91 50.79	3.05 3.05	16.97 17.00	93	193	260 (4.30)
XXVIII	$(CH_3)_2N$	NO_2	$C_{16}H_{16}N_4O_4$	328.31	58.53 58.40	4.91 4.91	17.06 16.80	83	185	304 (4.39)

The acylation of benzamide oximes occurs preferentially at the oxygen atom of the oxime group, which manifests itself usually by the presence in the i.r. spectra of a symmetrical and an antisymmetrical vibration bands of the NH_2 group [3, 4]. The i.r. spectra of all compounds show $\nu(NH_2)$ at 3500 and 3370 cm^{-1}, $\nu(C=O)$ at 1720 cm^{-1}, $\nu(C\equiv N)$ and $\nu(C=C)$ at 1640—1500 cm^{-1}, and ν(C—N) at 1265 cm^{-1} For compounds bearing an —NO_2 group, at ~1340 and 1525 cm^{-1}



Scheme 1

Table 2

Infrared absorption bands ($\tilde{\nu}$, cm^{-1}) for prepared substances in nujol mull

Compound	$\nu_{as}(NH_2)$	$\nu_s(NH_2)$	$\nu(C=O)$	$\nu(C=C)$; $\nu(C=N)$				ν(C—N)
I	3508	3389	1728	1615	1585	1565		1274
II	3499	3386	1725	1615	1580	1493		1271
III	3494	3376	1737	1619	1557	1517		1275
IV	3501	3388	1722	1615	1585			1267
V	3511	3416	1730	1605	1583			1244
VI	3505	3390	1724	1624	1595			1255
VII	3518	3423	1730	1600	1535			1265
VIII	3513	3414	1725	1620	1582	1515		1260
IX	3501	3345	1709	1620	1594	1517		1262
X	3505	3348	1711	1617	1592	1516		1260
XI	3507	3388	1720	1609	1584	1522		1260
XII	3489	3373	1717	1605	1580	1515		1253
XIII	3433	3338	1702	1632	1595	1520		1268
XIV	3478	3366	1714	1603	1580	1535		1258
XV	3508	3395	1725	1615	1585			1268
XVI	3513	3383	1735	1616	1595	1522		1273
XVII	3509	3383	1735	1658	1616	1592		1275
XVIII	3510	3393	1725	1613	1584			1268
XIX	3500	3388	1729	1670	1600	1520		1246
XX	3488	3353	1722	1627	1590	1532		1265
XXI	3508	3395	1720	1600	1538			1267
XXII	3508	3403	1725	1608	1585	1520		1253
XXIII	3479	3363	1721	1617	1607	1585		1269
XXIV	3483	3363	1722	1616	1587	1557,	1524	1270
XXV	3506	3397	1722	1608	1585	1559,	1526	1270
XXVI	3488	3390	1723	1608	1564	1522		1256
XXVII	3493	3366	1725	1627	1599	1532		1265
XXVIII	3489	3388	1716	1612	1576	1520		1276

were present intense bands corresponding to symmetrical and antisymmetrical vibrations of the NO_2 group.

To evaluate the polar effect of the substituents upon the location of the stretching vibrations of the NH_2 and $C=O$ groups i.r. spectra of the respective substances were measured in carbon tetrachloride and acetonitrile solutions. As can be seen from the data in Table 3 the effect of the amide oxime ring is not much pronounced. The low value of the tangency of the Hammett function (roughly 3.5 times smaller than that observed in the case of substituted benzophenones [10]) in the case of carbonyl vibration can probably be attributed to the lesser efficiency of the —C=N—O— group to transfer the polar effects. The Hammett dependence of the wavenumber of the stretching vibration of the amino group shows a negative tangency, as compared to that of substituted anilines [11]. As expected, the absolute value of the tangency increases 3—4 times when carbon tetrachloride is used as the solvent instead of acetonitrile, as a result of the more pronounced manifestation of the hydrogen bonding between the —NH_2 group and molecules of acetonitrile [12].

Table 3

The Hammett constants, wavenumbers (cm^{-1}) for the stretching vibrations of the NH_2 and $C=O$ groups, and statistical parameters of the correlation

Compound	σ_p	Measured in CCl_4			Measured in CH_3CN		
		$\nu_{as}(NH_2)$	$\nu_s(NH_2)$	$\nu(C=O)$	$\nu_{as}(NH_2)$	$\nu_s(NH_2)$	$\nu(C=O)$
I	0	3522	3423	1756	3487	3377	1742
II	0.227	3520	3421	1756	3480	3371	1741
III	0.232	3521	3421	1757	3483	3371	1742
IV	−0.17	3523	3423	1755	3488	3378	1740
V	−0.268	3523	3423	1754.5	3489	3379	1740
VI	0.778	3519	3420	1757		3370	1743
VII	−0.83	3524	3423	1751	3493	3383	1739
ϱ		−3.42	−2.20	3.81	−10.78	−9.29	2.59
ν_0		3522	3422	1755	3485	3376	1741
r		0.950	0.848	0.915	0.931	0.936	0.916
P		99	98	99	99	99	99
$s_{y,x}$		0.618	0.751	0.918	1.87	1.918	0.620

r — correlation coefficient.
P — probability level (%).
$s_{y,x}$ — rate of the decisive deviation for the point scattering around the regression line.

Experimental

O-Benzoylbenzamide oxime (*I*), *O*-benzoyl-4-bromobenzamide oxime (*III*), *O*-benzoyl-4-methylbenzamide oxime (*IV*) were prepared as described [1]. For the preparation of compounds *V* [2], *VI* [3], 4-chlorobenzamide oxime [13], and 4-dimethylaminobenzamide oxime [14] refer to the respective literature. Benzoyl chloride (Lachema, Brno), 4-chlorobenzoyl chloride (Fluka), 4-methoxybenzoyl chloride (Merck), and 4-nitrobenzoyl chloride (Koch-Light) were commercial products.

The electronic spectra were measured in ethanol and 50% (w/w) aqueous ethanol with a Unicam SP 1800 spectrometer using 1 cm cells. The stock solutions (10^{-4} M). were prepared by dissolving solid substances in ethanol.

The infrared spectra were measured in Nujol, carbon tetrachloride and acetonitrile (concentration of the solutions in the latter two cases was $\sim 10^{-2}$ M) with UR-20 (Zeiss, Jena) instrument. The spectrometer was calibrated with a polystyrene foil and indene.

O-Benzoylbenzamide oximes (II, VII—XXVIII)

A solution of 4-substituted benzoyl chloride (0.1 M) in pyridine (20 ml) was added dropwise and with cooling to a solution of 4-substituted benzamide oxime (0.1 M) in pyridine (200 ml) (anal. grade, Lachema, Brno). After 2 h the reaction mixture was poured into water (1 l) and the separated product was filtered, washed with water and crystallized (twice) from ethanol.

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