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Evaluation of the Effect of the Furazane Fragment on the NH Acidity of 4- and 5-Picrylaminobenzofurazanes in DMF and DMSO

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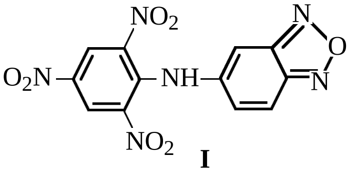
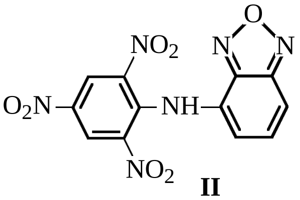
Abstract—The products of the reactions of picryl chloride with isomeric aminobenzofurazanes in DMF and DMSO were studied by means of nonaquoeus potentiometric titration. The effect of the position of the furazane fragment in 4- and 5-picrylaminobenzofurazanes on the NH acidity is considered. The electron-acceptor properties of the furazane fragment were evaluated via inclusion of the resulting data into the pK_a–σ correlation for 2,4,6-trinitrodiphenylamines. On this basis, conventional Hammett σ constants were calculated for the furazane fragment located in the immediate vicinity of the N-H center and one position distant from it.

The recent comparison of the NH acidity of furazane-containing nitroaromatic amines with that of related derivatives of 2,4-dinitro- and 2,4,6-trinitrodiphehylamines in DMF and DMSO revealed a stronger electron-acceptor power of the nitrobenzofurazanyl and dinitrobezofurazanyl fragments compared to the dinitrophenyl and picryl fragments, respectively [1, 2]. This fact provides indirect evidence to show that the furazane group in these compounds is a stronger electron acceptor that the nitro group. For a more comprehensive comparison we studied in the present work the NH acidity of 5- and 4-(picrylamino)benzofurazanes (**I**, **II**) in DMF and DMSO by means of potentiometry.



I



II

Compounds **I** and **II** were prepared by condensation of picryl chloride with 4- and 5-aminobenzofurazanes, respectively.

The resulting data were treated together with the acidity data for 2,4,6-tri- and 2,4,6,2'-, 2,4,6,3'-, and 2,4,6,4'-tetranitrodiphenylamines [3, 4]. The pK_a–σ correlation for 2,4,6-trinitro-3'(4')- R-diphenylamines [4] was also invoked. The resulting data (averaged over 8 measurements) are listed in the table together with the pK_a values for nitrodiphenylamines.

It can be seen that in DMF compounds **I** and **II** are stronger NH acids than the reference 2,4,6-trinitridiphenylamine. From that it follows that the furazane fragment exhibits a strong electron-acceptor effect that, at the same time, depends on the location of the substituent in the molecule. Compound **I** is a weaker acid than tetranitrodiphenylamines, while compound **II** is a stronger acid. As seen from the table, compound **I**

Relative acidity of picrylaminobenzofurazanes and nitrodiphenylamines in DMF and DMSO

Compound	pK_a (av.)	
	DMF	DMSO
5-Picrylaminobenzofurazane (**I**)	5.89	1.97
4-Picrylaminobenzofurazane (**II**)	5.18	1.10
2,4,6-$(NO_2)_3$-Diphenylamine	8.06 [4]	3.25[a]
2,4,6,2'-$(NO_2)_4$-Diphenylamine	5.66 [3]	1.74[a]
2,4,6,3'-$(NO_2)_4$-Diphenylamine	6.16 [3]	2.06[a]
2,4,6,4'-$(NO_2)_4$-Diphenylamine	5.55 [3]	1.68[a]

[a] Calculated from the correlation pK_a(DMF) = f[pK_a(DMSO)] (without data for 4'-$COCH_3$), n = 4.

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in which the furazane fragment is one position distant from the NH group exhibits a weaker acidity compared to compound **II** in which this fragment is adjacent to the NH center.

The acidity of both substances in a more basic DMSO is significantly higher than in DMF. In both cases, ΔpK_a is about 4 units. The same difference is also characteristic of previously studied reaction series in which a linear $pK_a(DMF) = f[pK_a(DMSO)]$ correlation was also revealed, implying a certain differentiating action of DMF compared to DMSO [1, 2, 4].

The correlation coefficient r calculated with all the previously studied compounds is 0.993 (n = 28). The correlation is not deteriorated by the inclusion of compounds **I** and **II** (r = 0.992, n = 30). Therewith, it is important to note that, as applied to 2,4,6-trinitrodiphenylamines [4], the correlations is slightly improved: r = 0.976 (n = 5) and r = 0.979 (n = 7). The lower correlation coefficient in the latter case is explained by the deviation of the value for the 4'-$COCH_3$ derivative for the linear dependence [4].

The interrelation of the pK_a data in DMF and DMSO for compounds **I** and **II** and for related compounds studied previously, as well as the evident structural similarity of compounds **I** and **II** and substituted 2,4,6-trinitrodiphenylamines, allowed us to include the results for **I** and **II** in the pK_a–σ correlation characteristic of the latter series [4]. In terms of this approach, the furazane fragment is considered as a two-positional analog of the nitro group as a very strong electron acceptor and thus is assigned a conventional σ constant.

The calculated σ_c values of the furazane fragment in compound **I** are 1.08 in DMF and 1.03 in DMSO. These values are in a good agreement with each other. The average σ_c is 1.05. This value is slightly higher that the half-sum of $\sigma_{p\text{-}NO_2}$ (1.27) and $\sigma_{m\text{-}NO_2}$ (0.71) that provide for the pK_a-σ correlation in the 2,4,6-trinitro-3'(4')R-diphenylamine series. This finding suggests that the acceptor power of the furazane fragment in compound **I**, that occupies simultaneously *meta* and *para* positions, is roughly half-sum of the acceptor powers of the 3'- and 4'-nitro groups in 2,4,6,3'- and 2,4,6,4'-tetranitrodiphehylamines. The correctness of this estimate is confirmed by the fact that the pK_a of compound **I** in DMF is approximately equal to the average pK_a of the above-mentioned tetranitrodiphenylamines (5.89 and 5.85, respectively). Moreover, in DMSO the pK_a half-sum criterion is fairly fulfilled (1.97 and 1.87).

The electron-acceptor power of the 2'-nitro group in 2,4,6,2'-tetranitrodiphenylamine is weaker that that of the 4'-nitro group in 2,4,6,4'-tetranitrodiphenylamine. This follows from a comparison of the pK_a values of these compounds (see table) and also from the pK_a-σ correlation [4] with the pK_a of 2,4,6,2'-tetranitrodiphenylamine included in the data set and resulting in σ_{NO_2} 1.20. In this connection, considering compound **II** as an analog of 2,4,6,2'- and 2,4,6,3'-tetranitrodiphenylamine reveals a significantly stronger and differentiated effect of the furazane fragment in this compound compared to compound **I**. The estimates for σ_c in **II** are 1.44 for DMF and 1.75 for DMSO. The significantly higher σ_c values for the furazane fragment in benzofurazane **II** compared to **I** give evidence for a strong interaction between the NH center and the furazane nitrogen atom, responsible for the high acidity of the former compound. The significant difference of the results for compound **II** in DMF and DMSO can be explained by a superposition of two factors: stronger specific interaction of the furazane fragment with the NH center in DMSO and lower sensitivity to the polar effect of the pK_a of 2,4,6-trinitro-3'(4')-R-diphenylamines in DMSO (ρ 1.21) compared to DMF (ρ 2.21) [4].

EXPERIMENTAL

The IR spectra were recoded on a Specord 75-IR spectrometer (KBr pellets, Vaseline oil). The ^1H NMR spectra were recorded on a Bruker AC-400 spectrometer (400 MHz) against DMSO-d_6 and $(CD_3)_2CO$.

Synthesis of (picrylamino)benzofurazanes *(general procedure)*. To a solution of 10 mmol of corresponding aminobenzofurazane [5, 6] in 20 ml of methanol, a solution of 10 mmol of picryl chloride in 20 ml of methanol and 10 mmol of triethylamine were added. The reaction mixture was refluxed for 2.5 h, cooled, and diluted with water. The precipitate that formed was filtered off, washed with water, ethanol, and ether, and dried.

5-(Picrylamino)benzofurazane (I). Yield 85%, mp 187–188°C (from methanol). IR spectrum, ν, cm^{-1}: 3380 (NH), 1535, 1330 (NO_2), 1615, 1290 (benzofurazane). Found, %: C 41.58, 41.74; H 1.62, 1.79; N 24.36, 24.41. $C_{12}H_6N_6O_7$. Calculated, %: C 41.62; H 1.73; N 24.28.

4-(Picrylamino)benzofurazane (II). Yield 83%, mp 155–156°C (from methanol). IR spectrum, ν, cm^{-1}: 3390 (NH); 1540, 1320 (NO_2), 1620, 1280 (benzofurazane), Found, %: C 41.49, 41.72; H 1.64, 1.71; N 24.42, 24.51. $C_{12}H_6N_6O_7$. Calculated, %: C 41.62; H 1.73; N 24.28.

The products were crystallized no less than 4–5 times from appropriate solvents and dried in a vacuum. The purity of the products was controlled by TLC on Sulufol UV-254 plates and by ^{1}H NMR spectroscopy. DMF and DMSO were purified according to [7].

Titration and calculation of the pK_a values were carried out according to the procedure in [3]. Statistical calculations were carried out using the Microsoft Excel program. The error in the measured $E_{1/2}$ values was no more than 0.5 mV and in the calculated pK_a values, ±0.02 units.

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