Pyrazoles X. The Resonance Interaction in 4-Nitro- and 4-Nitrosopyrazoles. Ionisation Constants, Ultraviolet and Visible Spectra (1)

Clarisse L. Habraken, C. I. M. Beenakker and J. Brussee

Gorlaeus Laboratories, The University, Leiden, Box 75, The Netherlands

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In continuation of our studies of the resonance interaction in 4-substituted pyrazoles (2,3) we have synthesized 3(5)-*t*-butyl-5(3)-methyl-4-nitrosopyrazole (**1**), 3,5-di-*t*-butyl-4-nitrosopyrazole (**2**), 3(5)-*t*-butyl-5(3)-methyl-4-nitropyrazole (**3**) and 3,5-di-*t*-butyl-4-nitropyrazole (**4**). In addition to our interest in the influence of *ortho* substituents on the interaction of the 4-nitro and the 4-nitroso group with the pyrazole ring, we were also interested in the resonance effect of the nitroso group in particular (4,5).

Contrary to nitroso benzenes, alkyl-substituted nitrosopyrazoles (6,7) exist primarily as monomers in the solid state and in solution. This appears from their blue or green color, the presence of a n $\rightarrow \pi^*$ band of low intensity. The existence of nitroso-compounds as monomers is generally ascribed to strong resonance interaction and steric hindrance of dimerization (4,8,9,10). Also, in contrast to the nitroso benzenes, the nitrosopyrazoles (**1**, **2**) and 3,5-dimethyl-4-nitrosopyrazole (**5**) are perfectly stable compounds which are not easily decomposed in acid media. The blue color, an absorption at such a short wavelength in the visible region as compared to nitrosobenzene, and the relative strong acidities indicate a distinct resonance interaction (see II) (8,9).

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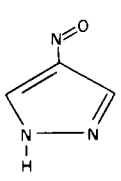

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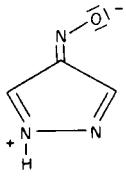

II

Earlier investigations showed that, in general, the 4-pyrazolyl group acts as an electron donating group (2). From the uv spectra and pK_a values we concluded the absence of a steric effect of *ortho* methyl groups in 4-nitropyrazoles (3). A study of the dipole moments of the same compounds corroborated this conclusion (11).

Replacement of the methyl groups by *t*-butyl groups in 4-nitro- and 4-nitrosopyrazoles (see Table I) decreases the acidity of these compounds as expected. In this instance the steric as well as the inductive effect of the *t*-butyl groups change the pK_a value in the same direction. An hypsochromic shift of the uv maximum, indicating a steric effect, is only found when the nitro- and the nitroso group, in each case, is flanked by two *t*-butyl groups.

Table I

p*K*a Values and UV Spectra of 4-Nitroso- and 4-Nitropyrazoles (λ max in nm)

No	Substituent	in H_2O		in 0.05 N HCl		in 0.05 N NaOH		
		λ max	(log ε)	λ max	(log ε)	λ max	(log ε)	pK_a
5(a)	3,5-dimethyl-4-NO-	307	(4.17)			319	(4.32)	9.14
1	3(5)-*t*-butyl-5(3)-methyl-4-NO-	310	(4.09)	309	(4.09)	323	(4.22)	9.18
2(b)	3,5-di-*t*-butyl-4-NO-	310	(4.05)	310	(4.05)	324	(4.16)	9.74
3	3(5)-*t*-butyl-5(3)-methyl-4-NO_2-	288	(3.86)	288	(3.87)	323	(4.03)	10.92
4(b)	3,5-di-*t*-butyl-4-NO_2			278	(3.73)	327	(4.06)	11.29

(a) See reference 5. (b) Due to poor solubility measured in 50% methanol.

Table II

Visible Spectra of 4-Nitrosopyrazoles (λ max in nm)

No	Substituent	in methanol		in benzene	
		λ max	(ε max)	λ max	(ε max)
5	3,5-dimethyl-	665	(57)	687	(93)
1	3(5)-*t*-butyl-5(3)-methyl-	676	(47)	692	(76)
2	3,5-di-*t*-butyl-	667	(41)	696	(63)

However, this effect would be small considering that the hypsochromic shift is accompanied only with a small decrease in the intensities.

In the case of 4-nitrosopyrazole a contribution of resonance form II may be quite important (9). This is shown by the shift of the visible absorption maximum ($n \rightarrow \pi^*$) on changing from methanol to benzene solution (see Table II). This is in concurrence with a decrease of the contribution of II since a change from a polar to a non-polar solvent would diminish the contribution of II. Steric inhibition of resonance would have the same effect. That is, a decreasing contribution of II which would shift the uv maximum ($\pi \rightarrow \pi^*$) to a shorter wavelength, would for that very reason shift the visible band ($n \rightarrow \pi^*$) to a longer wavelength. The fact that no such shift is found indicates rather the absence of a steric effect. Though, considering these effects, we have to bear in mind that even a fairly large deviation of coplanarity will not destroy the resonance interaction substantially (12). In conclusion, even the introduction of two *t*-butyl groups in the *ortho* positions of the 4-nitro and the 4-nitrosopyrazoles does not result in a considerable decrease of the strong resonance interaction of the nitro- and the nitroso group with the 4-pyrazolyl ring.

A comparison of the pK_a values of 4-nitro- and 4-nitrosopyrazoles shows that the nitroso group possesses a larger positive resonance effect then the nitro group. Lüttke *et al.*, came to the same conclusion in their comparative study of the structures of nitro- and nitrosodimethylamine (13). Formerly, in the literature, the directive effect of the nitroso group has been questioned (4). In an earlier publication (5) we have reported the Hammett substituent constant for the *para*-nitroso group (1.46 ± 0.03) computed from the pK_a values of **5** and of 4-nitro-, 3(5)-methyl-4-nitro- and 3,5-dimethyl-4-nitrosopyrazole (9.67; 10.06 and 10.65) respectively, and the *meta* substituent constant for methyl (-0.07) and the *para* substituent constant for nitro (1.26) (14). Taking the additional pK_a values for **1**, **2**, **3** and **4** and the substituent constant for *meta t*-butyl (-0.10) the Hammett substituent constant for the *para* nitroso group is found to be 1.47 ± 0.05 in perfect agreement with the value reported earlier (5).

EXPERIMENTAL

General.

Pivaloyl acetone and dipivaloylmethane were synthesized according to the procedures developed by Hauser *et al.* (15). All melting points are uncorrected. Elemental analyses were performed by Mr. W. J. Buis, TNO laboratories, Utrecht, The Netherlands. All spectra were taken at room temperature with a Perkin Elmer 137UV spectrophotometer.

The spectra of the conjugate bases were determined in aqueous sodium hydroxide (0.05 *N*), those of the neutral molecules were determined in aqueous hydrochloride (0.05 *N*). The spectra of equilibrium mixtures of the neutral molecule and its conjugate base were measured in buffer solutions prepared as described by Sörensen (16). The equilibrium between the neutral molecule and the conjugate base of the compounds investigated gives rise to a set of absorption curves with an isobestic point. From these spectra pK_a values were calculated using optical densities at maximum wavelength of the neutral molecule and of its conjugate base. No corrections were applied to obtain thermodynamic ionisation constants.

3(5)-*t*-Butyl-5(3)-methyl-4-nitrosopyrazole (**1**).

A solution of 1.4 g. of sodium nitrite in 2 ml. of water was slowly added to a stirred solution of 2.8 g. of pivaloylacetone in 6 ml. of acetic acid. During the addition the mixture was chilled in ice water. After standing at room temperature for some time, a solution of 1.1 g. of hydrazine hydrate in 2 ml. of water was slowly added. Almost immediately a thick blue precipitate appeared. After standing for an hour this precipitate was collected on a Hirsch funnel, washed with water and dried (2.8 g.). Crystallization from benzene afforded 2.1 g. (64%), m.p. 164°.

Anal. Calcd. for $C_8H_{13}N_3O$: C, 57.46; H, 7.84; N, 25.13. Found: C, 57.76; H, 7.96; N, 25.10.

3,5-Di-*t*-butyl-4-nitrosopyrazole (**2**).

A mixture of 4 g. of dipivaloylmethane, 3 g. of *n*-amylnitrite and 4 drops of concentrated hydrochloric acid was allowed to stand overnight at 0°. A precipitate, if formed, was filtered off and a solution of 3 ml. of hydrazine hydrate in 20 ml. of acetic acid was added to it. After standing for two hours at room temperature the precipitate was filtered off, washed with 5 ml. of acetic acid and finally crystallized from ethanol/water; 1.6 g. (46%), m.p. 206-208°.

Anal. Calcd. for $C_{11}H_{19}N_3O$: C, 63.12; H, 9.15; N, 20.08. Found: C, 63.09; H, 9.06; N, 20.07.

3(5)-*t*-Butyl-5(3)-methyl-4-nitropyrazole (**3**).

To a solution of 2.5 g. of 3(5)-*t*-butyl-5(3)-methylpyrazole (17) in 5 ml. of concentrated sulfuric acid was added successively 3 ml.

of nitric acid (d=1.4) and 10 ml. of concentrated sulfuric acid. After standing overnight the reaction mixture was heated on a water bath for 2 to 3 hours. Then the reaction mixture was poured on ice. The product was collected by filtration and crystallized from water, 2.4 g. (72%), m.p. 148°.

Anal. Calcd. for $C_8H_{13}N_3O_2$: C, 52.44; H, 7.15; N, 22.94. Found: C, 52.55; H, 7.10; N, 22.77.

3,5-Di-*t*-butyl-4-nitropyrazole (**4**).

One g. of 3,5-di-*t*-butylpyrazole, m.p. 186-187°, obtained in the usual way by condensation of dipivaloylmethane and hydrazine in acetic acid/hydrochloric acid solution, was dissolved in 2 ml. of sulfuric acid. To this solution was added 2 ml. of nitric acid (*d*=1.4), followed by 4 ml. of sulfuric acid. After standing overnight the reaction mixture was heated on a water bath for 4 hours, cooled and poured on ice. The precipitate was filtered off and crystallized from ethanol/water: 0.9 g. (74%), m.p. 205-208°.

Anal. Calcd. for $C_{11}H_{19}N_3O_2$: C, 58.64; H, 8.50; N, 18.65. Found: C, 58.65; H, 8.49; N, 18.40.

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