[CONTRIBUTION FROM THE COLLEGE OF PHARMACY OF THE UNIVERSITY OF CALIFORNIA]

THE DIPOLE MOMENTS AND STRUCTURE OF 2-NITRIMINOIMIDAZOLIDINE AND "1-NITRO-2-NITRAMINO-Δ^2-IMIDAZOLINE"

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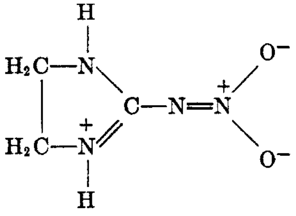
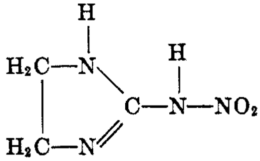
In a recent paper McKay, Picard, and Brunet (1) interpreted the ultraviolet spectra to indicate that 2-nitriminoimidazolidine and "1-nitro-2-nitramino-Δ^2-imidazoline" exist mainly as resonance hydrids of "zwitterion" forms, such as I etc., and that the compounds should not be classified as nitrimines. Contrary to this conclusion, Barton, Hall, and Wright (2) have given evidence that 2-nitriminoimidazolidine is a nitrimine. A decision between these two structures can be obtained from the dipole moments of the compounds. Calculations show that if the compounds are "zwitterions" or resonance hybrids of "zwitterions" they will have dipole moments of 15 to 25 D, while, if they are not, their dipole moments will be less than 10 D.



I



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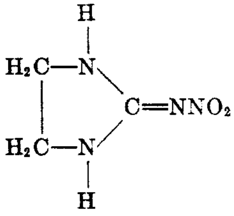

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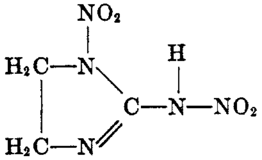

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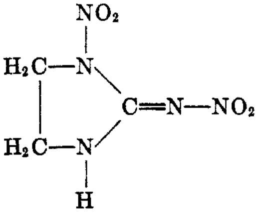

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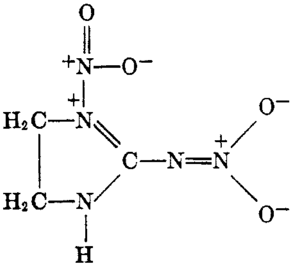

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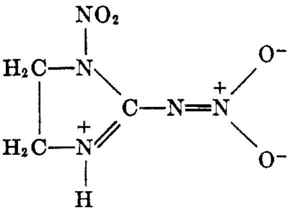


VII

The dipole moments of the compounds have been measured in dioxane solution at 30°. The compounds, of high purity, were supplied to us by Professor George F Wright. Their melting points were as follows: 2-nitriminoimidazolidine, m.p. 220.4–221.4° (dec.) soft at 219°; "1-nitro-nitramino-Δ^2-imidazoline", m.p. 151.0–151.3° (dec.) soft at 148°. The dioxane was purified as before (3). The plots of ϵ_{12} *versus* ω_2 were straight lines. The values of ϵ_1 and v_1 were obtained by extrapolation. The values of P_{E_2} were obtained from the molar refractivities of the groups. The dipole moments were calculated using the method of Halverstadt and Kumler (4).

$$p_{2_0} = \frac{3\alpha v_1}{(\epsilon_1 + 2)^2} + (v_1 + \beta)\frac{(\epsilon_1 - 1)}{(\epsilon_1 + 2)}$$

$$P_{2_0} = p_{2_0} M_2$$

$$\mu = 0.01281\sqrt{(P_{2_0} - P_{E_0})T}$$

The following values were found:

2-NITRIMINOIMIDAZOLIDINE

ω_2	ϵ_{12}	v_{12}
0.000195	2.2166	
.000431	2.2285	
.000603	2.2359	
.000770	2.2441	
.000207		0.97375
.000316		.97370
.000402		.97366
.000497		.97362
.000589		.97359

ϵ_1	α	v_1	β	P_{2_0}	P_{E_2}	μ
2.2076	47.25	0.97384	−0.433	1003.2	31.5	6.93

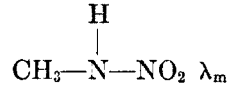
"1-NITRO-2-NITRAMINO-Δ^2-IMIDAZOLINE"

ω_2	ϵ_{12}	v_{12}
0.000246	2.2165	0.97374
.000386	2.2225	.97367
.000638	2.2331	.97358
.000850	2.2415	.97349

ϵ_1	α	v_1	β	P_{2_0}	P_{E_2}	μ
2.2071	41.00	0.97383	−0.408	1213.5	38.1	7.65

The observed dipole moments of 6.93 and 7.65 D for these compounds indicate that neither exists as a "zwitterion" or mainly as a resonance hybrid of "zwitterions" as has been concluded by McKay, *et al.* (1).

The other probable structures for 2-nitriminoimidazolidine are II and III.

Structure II is ruled out on a basis of both the acid strength and the ultraviolet spectrum. Structure II would have a pK_a in the range 3–5, while the observed pK_a is around 14 (2). The ultraviolet spectrum of the compound has a λ_{max} of 267 mμ and an ϵ_{max} of 17,700 (1). This absorption is at considerably longer wave length and has higher extinction than the sum of the absorption of a simple nitramine  $\mathrm{CH_3{-}\overset{\overset{\textstyle H}{|}}{N}{-}NO_2}$ λ_{max} 230 mμ, ϵ_{max} 7000 (5) plus guanidine hydrochloride, which has virtually no absorption above 230 mμ (6). This indicates conjugation is present between the nitro group and the rest of the molecule which is not consistent with structure II.

Structure III is an analog of urea and since the $=N-NO_2$ group is of about the same electronegativity as a $=O$ the compound would be expected to have approximately the same pK_a and pK_b as urea, which is the case. The compound is both a very weak acid and a very weak base, differing but little in this respect from water so structure III is consistent with the dissociation constants of the compound.

Structure III has the nitro group conjugated and is consistent with the ultraviolet spectrum of the compound.

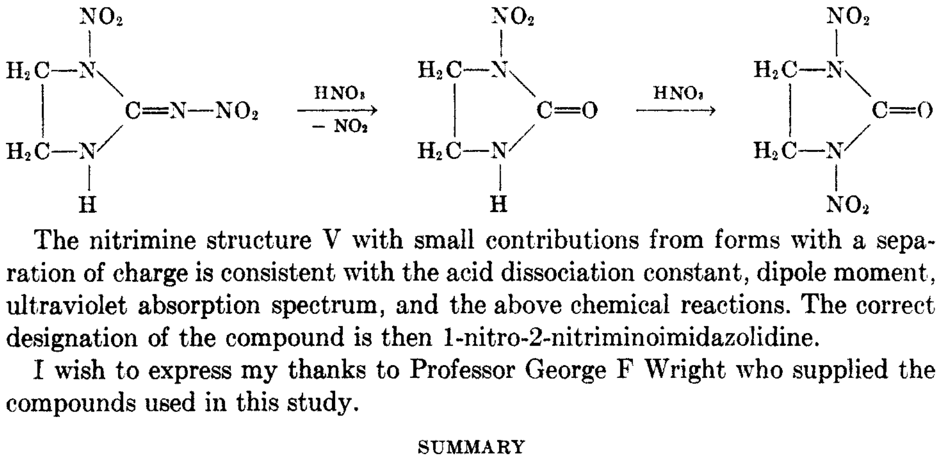
Calculations show that structure III would have a dipole moment of about 5 D, so small contributions from forms with a separation of charge such as I, etc. would be necessary to bring the moment up to the observed value of 6.93 D. The structure of the compound is mainly III so it should be classified as a nitrimine in agreement with the conclusions of Barton, Hall, and Wright (2) but contrary to the conclusions of McKay, *et al.* (1). The conclusions of the latter arise from a misinterpretation of the ultraviolet spectra which has been discussed in the preceding paper by Kumler and Sah.

The compound "1-nitro-2-nitramino-Δ^2-imidazoline" might have structure IV or structure V. If it has the latter, the correct name would be 1-nitro-2-nitriminoimidazoline. Structure IV is not consistent with the acid dissociation constant or the ultraviolet spectrum of the compound. The compound has pK_a 6.3 as the curve of Barton, Hall, and Wright (2) indicates. Structure IV would have pK_a 1–3. The spectrum λ_{max} 270 mμ, ϵ_{max} 13,300 (1) indicates the nitro group is conjugated which is not the case in structure IV.

Structure V is consistent with the dissociation constant, ultraviolet absorption spectrum, and dipole moment of the compound. The introduction of the additional nitro group in position 1 should bring about a large increase of the acidity of this compound over compound III because of three effects: the electronegativity of the NO_2 group; the fact that the undissociated molecule no longer has two resonating forms of equal energy; the fact that the plus charge in the forms with a separation of charge are confined to one  $\mathrm{{-}\overset{\overset{\textstyle H}{|}}{N}{-}}$ group. Each of these effects were operative to a much lesser extent in going from nitroguanidine to nitroaminoguanidine where the substitution increased the acidity by about 3.5 pK_a units. The much larger effect of the nitro group is adequate to increase the acidity by 7.7 pK_a units in going from III to V. Form VI makes virtually no contribution due to the plus charges on adjacent nitrogen atoms so VII will be the contributing form with a separation of charge.

Structure V has a nitro group conjugated so it accounts for the ultraviolet spectrum. The dipole moment is consistent with the major contribution from V plus small contributions from VII.

Although the facts that the compound gives a positive Franchimont test with dimethylaniline, loses nitrous oxide in an acidic nitration medium, and reacts with diazomethane have been given as evidence of the nitramine structure IV, it is doubtful if any of these tests are truly diagnostic of a nitramine. A hydrogen of sufficient acidity appears to be all that is necessary for reaction with diazomethane. The reactions below would seem to account just as well for the observed behavior in nitric acid. The Franchimont test would be expected to take place with any molecule giving nitrous acid under the conditions of the test, which seems possible for V as well as IV.



The nitrimine structure V with small contributions from forms with a separation of charge is consistent with the acid dissociation constant, dipole moment, ultraviolet absorption spectrum, and the above chemical reactions. The correct designation of the compound is then 1-nitro-2-nitriminoimidazolidine.

I wish to express my thanks to Professor George F Wright who supplied the compounds used in this study.

SUMMARY

The dipole moment of 6.93 D, acid strength, and ultraviolet spectrum of 2-nitriminoinidozolidine are consistent with the compound being a nitrimine as suggested by Barton, Hall, and Wright (2). The findings are contrary to both conclusions of McKay, Picard, and Brunet (1) that the compound is not a nitrimine, and that it is a resonance hydrid of "zwitterions".

The dipole moment of 7.65 D, pK_a of 6.3, and ultraviolet spectrum of "1-nitro-2-nitramine-Δ^2-imidazoline" indicate this compound is also a nitrimine and should be named 1-nitro-2-nitriminoimidazolidine. Both compounds probably have small contributions from forms with a separation of charge.

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REFERENCES

(1) McKay, Picard, and Brunet, *Can. J. Chem.*, **29**, 746 (1951).
(2) Barton, Hall, and Wright, *J. Am. Chem. Soc.*, **73**, 2201 (1951).
(3) Kumler and Halverstadt, *J. Am. Chem. Soc.*, **63**, 2182 (1941).
(4) Halverstadt and Kumler, *J. Am. Chem. Soc.*, **64**, 2988 (1942).
(5) Jones and Thorn, *Can. J. Research*, **B 27**, 836 (1949).
(6) *International Critical Tables*, **V**, 367, McGraw-Hill Book Co., New York.