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"ISONITRAMINES": NITROSOHYDROXYLAMINES OR HYDROXYDIAZENIUM OXIDES?

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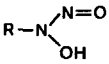
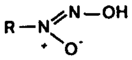
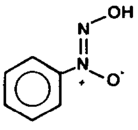
Summary: In the crystalline state and in solution isonitramines are hydroxydiazenium oxides.

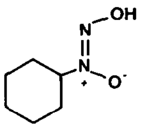
It is generally accepted today[1] that isonitramines[2] must be described by the nitrosohydroxylamine structure 1[3] rather than the isomeric hydroxydiazenium oxide structure 2[4]:

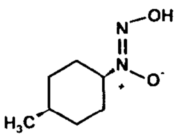

1


2

We now present evidence[5] that three isonitramines investigated by us (2a: R = phenyl[6], 2b: R = cyclohexyl[7], 2c: R = cis - 4 - methylcyclohexyl[8]) correspond to structure 2:


2a


2b


2c

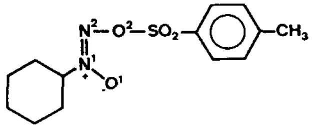
This structural assignment is based on X-ray structure analyses performed with single crystals of 2a and 2c and on UV and ^{13}C NMR spectroscopic data obtained from solutions of 2b and 2c.

X-ray structure analyses of 2a and 2c

X-ray intensity measurements[9] were performed with single crystals of 2a and 2c[10] cooled to -60 °C[11]. The structures were determined by direct methods, and all hydrogen atoms were located in difference maps[12]. Refinement proceeded until R = 0.045 (2a) and R = 0.053 (2c)[13]. The structures found by these analyses[14] are shown in the Figure below.

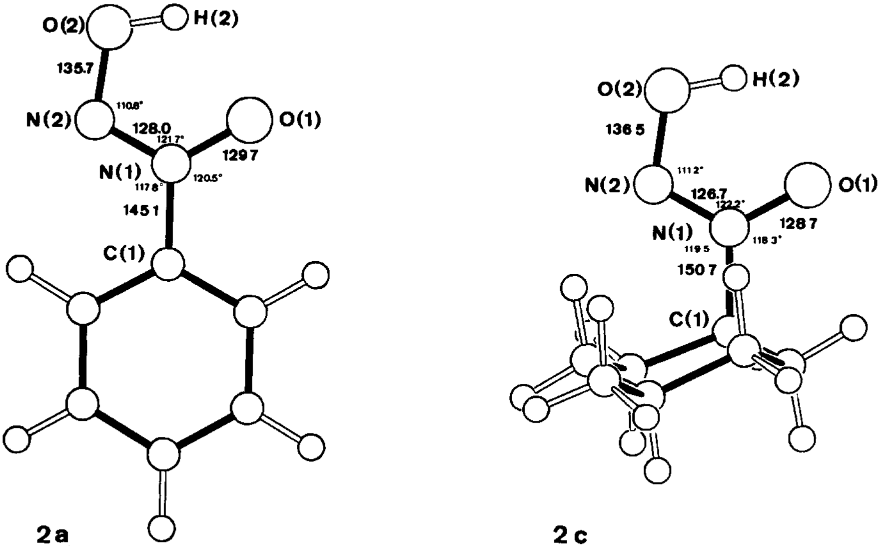
In both isonitramines all atoms of the N_2O_2H groups are coplanar. In 2a the dihedral angle between the aromatic ring and the substituent ("best planes") was found to be 3.4°. The cis - 1,4 disubstituted cyclohexane derivative 2c is fixed in the (1a, 4e) - conformation.

2a and 2c both have N(1) - N(2) double bonds. The N(2) - O(2) bonds[15] are considerably longer than the N(1) - O(1) bonds. Similar bond patterns were found in the diazeniumdioxy tosylate 3[16] by X-ray structure analysis[5]:



N(1) - N(2): 125.6 pm
N(2) - O(2): 141.3 pm
N(1) - O(1): 123.5 pm

3



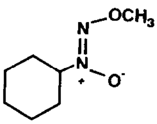
2a 2c

Figure: 2a and 2c with relevant bond distances and bond angles

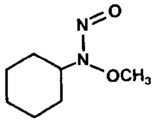
These findings rule out the nitrosohydroxylamine structure 1. They prove that the isonitramines 2a and 2c exist as (Z) - configurated hydroxydiazenium oxides in the solid state.

UV and ^{13}C NMR spectroscopic analyses of 2b and 2c

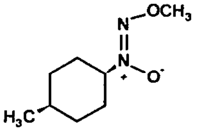
For structure correlations by UV and ^{13}C NMR spectroscopy the O-methyl derivatives of 2b (4 and 5) and of 2c (6 and 7) were prepared[17]:



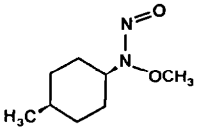
4



5



6



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UV spectra[18] of solutions of 2b and 2c (in cyclohexane, diethylether, acetonitrile, ethanol), and of 4 and 6 are similar and show π-π^* absorption bands only (see Table).

compounds	$\pi-\pi^*$ UV bands		$n-\pi^*$ UV bands		^{13}C NMR chemical shifts (ppm)					
	λ_m (nm)	ϵ_m	λ_m (nm)	ϵ_m	ring carbon atoms				C-methyl	O-methyl
					C(1)	C(2,6)	C(3,5)	C(4)		
2b	228.5	7200	-	-	71.1	30.1	24.4	25.0	-	-
4	234.8	9180	-	-	72.5	30.6	24.7	25.2	-	60.2
5	235.8	6050	354.9	71.4	63.9	30.8	25.2	25.3	-	63.5
2c	228.3	6360	-	-	69.2	29.9	26.6	29.5	20.1	-
6	235.2	8700	-	-	70.9	30.0	26.6	28.7	19.5	60.1
7	(235.4)[19]		(354.5)[19]		62.3	30.5	26.9	29.3	19.6	62.9

Table: Spectroscopic data of 2b and 2c and their O-methyl derivatives

UV: ethanol solutions; ^{13}C NMR: benzene solutions, shifts relative to internal TMS

5 and 7 exhibit the $n-\pi^*$ bands of the N-nitroso groups[20] in addition to the $\pi-\pi^*$ bands. Analogous observations have been made with methylene diisonitramine (Traube's compound[2]) and its O-methyl derivatives[21,22].

The absence of $n-\pi^*$ bands in the UV spectra of isonitramines has been tentatively attributed to intramolecular[21] and/or intermolecular[23] hydrogen bonding in 1. Since structure 2 would also fit the UV data ^{13}C NMR spectra[24] were taken in order to obtain additional information. As follows from the Table the same two groups of compounds found by UV spectroscopy are also observed by ^{13}C NMR spectroscopy: The resonance signals of the N substituted ring carbon atoms C(1) of the isonitramines 2b and 2c occur close to the corresponding signals of the diazeniumdioxy compounds 4 and 6, respectively. In contrast, the signals of C(1) of the nitrosohydroxylamines 5 and 7 are considerably displaced to higher fields.

The small differences in shift (1.6 to 1.9 ppm) between the cyclohexyl derivatives 2b, 4 and 6 and the corresponding cis - 4 - methylcyclohexyl homologs can be explained in terms of a significant contribution of the (1a, 4e)- conformer in the conformer equilibrium[25] of the latter ^{13}C NMR spectra of 2b and 2c exhibit narrow lines when taken at room temperature (methanol solutions). When measurements are performed at -70 °C line broadening is observed in the spectrum of 2c only. Since freezing of the tautomer equilibrium $1 \rightleftharpoons 2$ should occur with both isonitramines the observed line broadening must be attributed to freezing of a conformer equilibrium[26] $(1e, 4a) \rightleftharpoons (1a, 4e)$.

We conclude that the UV and ^{13}C NMR data of the two isonitramines investigated in solution are both compatible with the hydroxydiazenium oxide structures 2b and 2c.

Acknowledgement. We thank Dr. W. Bremser of BASF Aktiengesellschaft for help with the interpretation of the NMR spectra.

References and Notes

+) Dedicated to Prof. Dr. H. Pommer on the occasion of his sixtieth birthday.

1. Cf. eg. B. Zeeh, H. Metzger, "Methoden der Organischen Chemie (Houben-Weyl", (E. Müller, ed.), 10/1, 1273 - 1279 (1971).
2. This name was coined by W. Traube, Ann. Chem., 300, 81 (1898).
3. Cf. A. Wohl, Chem. Ber., 27, 1432 (1894).
4. Cf. A. Angeli, ibid., 29, 1884 (1896); Gazz. Chim. Ital., 46/2, 67 (1916).
5. Experimental details will be given in the full paper (in preparation).
6. C. S. Marvel, Org. Synth., Coll. Vol., 1, 177 (1948).
7. M. Pape, P. Raff, German Patent 1 543 376.
8. 2c (b.p.$_{0.2}$: 53 - 58 °C) was prepared from 4 - methylcyclohexanone oxime (O. Wallach, Ann. Chem., 346, 249 (1906) via catalytical hydrogenation (cf. W. E. Rosen, M. J. Green, J. Org. Chem., 28, 2797 (1963) and nitrosation (cf. H. Metzger, German Patent 1 019 657). All new compounds had correct elemental composition.
9. Synthex P2$_1$ diffractometer, Cu K$_\alpha$ radiation, graphite monochromator.

10. Single crystals of 2a (0.3 x 0.33 x 0.2 mm) and 2c (0.45 x 0.3 x 0.2 mm) were obtained by sublimation (0.2 torr, 20 °C).
2a crystallizes in the orthorhombic space group $P2_12_12_1$; a = 485.02(2) pm, b = 1056.4(1) pm, c = 1221.2(1) pm, Z = 4. The intensities of 769 independent reflections were collected (2 of them with $I < 2\sigma_I$ were not included in the refinement) with $\Theta/2\Theta$ scans and analyzed by a Lehmann-Larson algorithm.
2c yielded crystals in the monoclinic space group $P2_1/c$; a = 1162.7(2) pm, b = 536.8(1) pm, c = 1379.9(3) pm, β = 105.80(2) °, Z = 4. 1041 independent reflections (87 with $I < 2\sigma_I$) were measured and analyzed as above.
2b yielded twinned crystals only.

11. So far, the inadequate stability of the isonitramines has hampered structure elucidation by X-ray structure analysis; cf. J. H. Bryden, Acta Crystallogr., 12, 581 (1959).

12. The hydroxyl hydrogen (H(2) in the Figure) appeared with a density of 0.4 x 10^{-6} e pm^{-3} (spurious maxima < 0.3 x 10^{-6} e pm^{-3}) in 2a and with 0.5 x 10^{-6} e pm^{-3} (< 0.2 x 10^{-6} e pm^{-3}) in 2c.

13. R_w = 0.046 with g = 0.000 065 (2a) and R_w = 0.059 with g = 0.000 06 (2c). $R_w = \Sigma w^{1/2}\Delta / \Sigma w^{1/2}|F_o|$ with $w = 1/(\sigma^2_{(F_o)} + g F_o^2)$.

14. The standard deviations of the bond lengths shown in the Figure are 0.2 - 0.3 ppm. The bond distances of 2c have been corrected for molecular thermal motions according to V. Schomaker, K. N. Trueblood, Acta Crystallogr., Sect. B., 24, 63 (1968).

15. In 1 a N(2) - O(2) bond distance might be expected similar to that found in dimethylnitrosamine (126.0(6) pm; B. Krebs, J. Maudt, Chem. Ber., 108, 1130 (1975)); cf. also P. Rademacher, R. Stølevik, W. Lüttke, Ang. Chem., 80, 842 (1968).

16. 3 (m.p.: 92 - 3 °C) was prepared from the potassium salt of 2b by reaction with tosyl chloride in DMSO.

17. 4 (b.p.$_{14}$: 124 °C) and 6 (b.p.$_{0.1}$: 80 °C) were obtained by decomposing the tosylates of 2b and 2c, respectively, with sodium methoxide; cf. J. P. Freeman, L. D. Lillwitz, J. Org. Chem., 35, 3107 (1970). 5 (b.p.$_{0.5}$: 80 - 2) was prepared from cyclohexanone oxime via O - methylation, catalytical hydrogenation and nitrosation (cf. note 8.). A mixture of 7 and 6 was obtained from the silver salt of 2c by methylation with methyl iodide in diethyl ether (cf. note 2).

18. Zeiss Spektralphotometer DMR 22.

19. 7 has not yet been obtained in a pure state.

20. Cf. C.N.R. Rao, K. R. Bhaskar, "The Chemistry of the Nitro- and Nitroso Groups" (H. Feuer, ed.) part 1, pp. 152 - 155 (1969).

21. R. N. Jones, G. D. Thorn, Can. J. Res., Sect. B, 27, 828 (1949)

22. M. Piskorz, T. Urbański, Bull. Acad. Pol. Sci., Sér. Sci. Chim., 11, 597 (1963).

23. R. N. Haszeldine, J. Jander, J. Chem. Soc., 691 (1954).

24. Bruker WH-270.

25. Conformational analysis of cyclohexane derivatives by NMR spectroscopy is discussed by H. Feltkamp, N. C. Franklin, Ang. Chem., 77, 798 (1965); cf. E. L. Eliel, Ang. Chem., 77, 784 (1965).

26. In solution the monosubstituted cyclohexane derivatives 2a, 4 and 6 should exist almost exclusively in the (1e) - conformation (see note 25.).

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