310. Concerning the Hydroxyazo-Quinonehydrazone Equilibrium of a Trisazonaphthalene with an [18]Annulene Perimeter Macrocyclic Aza Compounds, III[1])

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Summary. The hydroxyazo-quinonehydrazone equilibrium of the cyclic trisazonaphthalene **1** has been determined from the ^{1}H-NMR. spectrum of the ^{15}N-labelled compound. The size of the coupling constant $J_{^{15}\mathrm{N},\mathrm{H}}$ demonstrates that the equilibrium of **1** with respect to the non-cyclic reference compound **6** is shifted towards the hydroxyazo form by factors of at least 5.1 and 3.9 in DMSO and H_2O, respectively.

1. Introduction. – Our continued interest in macrocyclic azo compounds[2]) led us to consider the trisazonaphthalene **1** which has been synthesized by *Allan et al.* [2]. The macrocycle **1** may formally be regarded as an annelated derivative of the hypothetical hexaaza[18]annulene **2**. Representatives of this class of π-equivalent azaannulenes are of interest principally because, in contrast to π-excessive azaannulenes they are virtually unknown[3]).

In carbocyclic and π-excessive benzoannulenes and annulenes fused to naphthalenes and higher benzenoid π-electron systems the diatropism of the parent compound is reduced or even quenched completely by annelation[4]). The closest known carbocyclic analogue to the trisazonaphthalene **1** is the trisdehydro[18]annulene **3** which, in contrast to its parent compound **4**, does not sustain a diamagnetic ring current [4]. However, the electronic spectrum of **3** is very similar to that of diatropic **4**[5]). Thus, the macrocyclic perimeter of **1** would be expected to be atropic. But the electronic spectrum is consistent with the cyclic chromophore [2].

2. Problem. – We were interested in determining whether or not the hydroxyazo-quinonehydrazone equilibrium of **1** is dominated by the hydrazone tautomer as is the case for azonaphthols in general and particularly for 2-phenylazo-1-naphthols **5** [5] [6 and references therein]. If it is assumed that delocalization of π-electrons – to whatever degree – in the macrocyclic perimeter of **1** is rendered more difficult in the hydrazone tautomer, the tautomeric equilibrium should be shifted towards the hydroxyazo form, provided the 18-membered perimeter significantly contributes to the π-electron energy. To detect such a contribution, a knowledge of the equilibrium position of an acyclic reference compound is required. For this purpose the bisazonaphthalene **6**, which most probably has the conformation shown below, was chosen.

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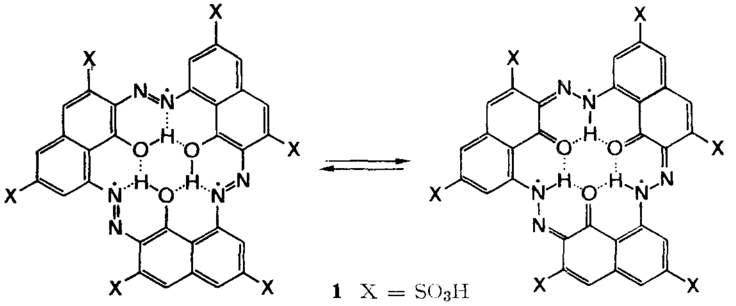
[1]) Part II: see [1].

[2]) See [1].

[3]) Porphyrines and phthalocyanines are diatropic hybrids between π-equivalent and π-excessive electron systems in the sense that both their 18- and 16-membered perimeters contribute to their delocalized electronic ground states. For a recent review see [3].

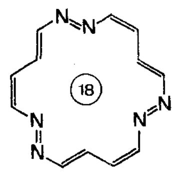
[4]) See [3] and references therein.

[5]) This of course is no contradiction, since two different probes for the electronic structure are used.



1 X = SO_3H

2



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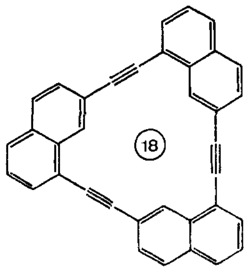

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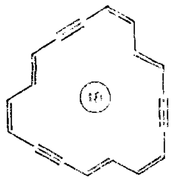
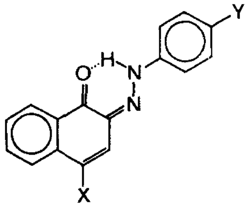


To determine the equilibrium positions of **1** and **6** we used as a criterion the size of the coupling constant $J_{^{15}N,H}$ [7]. This is not the most sensitive technique, but other spectroscopic methods (*e.g.* UV./VIS. spectroscopy) require derivatives of both tautomers which were unavailable[6]).

HMO calculations did not indicate a significant contribution of the macrocyclic perimeter to the π-electron energy of **1**[7]). Its ^1H-NMR. spectrum had been assigned on the basis of chemical shifts to the pure hydrazone [2]. However, the arguments were not convincing.



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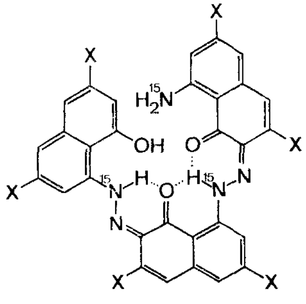
X = H, SO_3H
Y = H, OCH_3, Cl, SO_3H, CF_3



6
X = SO_3H

3. Syntheses. – The macrocycle **1** (*N = ^{15}N) and the reference compound **6** were synthesized from ^{15}N-labelled 1,8-aminonaphthol-3,6-disulfonic acid according to the method of *Allan et al.* [2][8]). ^{15}N-1,8-Aminonaphthol-3,6-disulfonic acid was obtained according to known methods [8] using ^{15}N-nitric acid.

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[6]) For a detailed discussion see [6].

[7]) We thank Prof. *F. Gerson* (Universität Basel) for these calculations.

[8]) *We wish to thank Dr. Z. J. Allan for his personal advice during his stay in our laboratory.*

Table 1[9]. *^{1}H-NMR. data of* **1** *in DMSO-d_6 and H_2O*

Solvent	**1**	δ_{NH}	$J_{^{15}N,H}$
DMSO-d_6	^{14}N	16.43	–
	^{15}N	16.30	95.0
H_2O	^{14}N	16.36	–
	^{15}N	16.38	96.5

Table 2. *^{1}H-NMR. data of* **6** *in DMSO-d_6 and H_2O*

Solvent	**6**	δ_{NH}	$J_{^{15}N,H}$
DMSO-d_6	^{14}N	16.75, 17.15	–
	^{15}N	16.45, 16.75	101.0, 100.1
H_2O	^{14}N	16.86	–
	^{15}N	16.96	101.0

4. Results and Discussion. – The relevant ^{1}H-NMR. data of labelled and unlabelled trisazonaphthalene **1** are summarized in Table 1. The observed coupling constants correspond within the limit of error to the typical value of 96 Hz for a ^{15}N–H bond of an sp^2-hybridized nitrogen atom [7]. Furthermore we note that the coupling constants in the reference compound **6** (Table 2) exceed this typical value by *ca.* 4–5 Hz. This difference we attribute to well established solvent and substituent effects[10]. If the experimental error of ±1.2 Hz is taken into account, the coupling constant in **6** may be as large as 102.2 Hz. If this value corresponds to 100% hydrazone of our model compound **6** and therefore of the macrocycle **1**, we can calculate using equation (1) [9] and an average coupling constant $J_{^{15}N,H} = 100.7$ Hz (observed) that **6** exists as at least 98.5 (±1.1)% hydrazone in both solvents. Similarly the coupling constants of the macrocycle **1** correspond to a small solvent dependent shift of the equilibrium to 93.0 (±1.0) and 94.4 (±1.0)% hydrazone in DMSO and H_2O, respectively.

$$J_{obs}/J_{^{15}N,H} \cdot 100 = \%\ \text{hydrazone} \qquad (1)$$

$$K_T = \frac{[\text{Azo}]}{[\text{Hydrazone}]} = \frac{J_{^{15}N,H} - J_{obs}}{J_{obs}} \qquad (2)$$

The same assumptions and use of equation (2) [10] lead to $K_{T(DMSO, H_2O)} \leqslant 1.5 \cdot 10^{-2}$ for **6**, whereas for **1** $K_{T(DMSO)} = 7.6 \cdot 10^{-2}$ and $K_{T(H_2O)} = 5.9 \cdot 10^{-2}$. Thus the tautomeric equilibrium of **1** is shifted towards the hydroxyazo form by factors of *ca.* 5.1 and 3.9 with respect to the reference compound **6**. It is tempting therefore to conclude that the contribution of the macrocyclic perimeter to the π-electron energy of **1** is of the order of 3.5–4.1 kJ mol^{-1} (*ca.* 0.9 kcal mol^{-1}). Provided of course that our assumptions are correct and the observed shifts are not the result of employing a model which is too crude, the above factors represent minimum values. Even so, we should point out that in agreement with expectations the contribution of the 18-membered perimeter to the π-electron energy is virtually negligible.

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[9] Tables 1 and 2: Chemical shifts in ppm from internal TMS; coupling constants in ± 1.0 Hz (Table 1), ± 1.2 Hz (Table 2); H_2O solutions contained *ca.* 10% DMSO-d_6 for locking.

[10] See [7] and references therein.

Experimental Part

General. ^{1}H-NMR. spectra were recorded on *Varian* XL-100 (*Varian AG*, Zug) and *Bruker* WH-90 (Technisch-Chemisches Laboratorium, ETHZ) FT-spectrometers using saturated solutions (*ca.* 2–4 mg/0.5 ml). For labelling purposes 14.8 M nitric acid of 99% ^{15}*N*-isotopic purity (*Stohler Isotope Chemicals*, Innerberg) was used. Paper chromatography was carried out on *Wathman* No. 1 paper using isoamylalcohol/pyridine/10% NH_4OH 1:1:1 as eluent.

^{15}*N-1,8-Aminonaphthol-3,6-disulfonic acid* (*H-acid*). H-Acid was synthesized according to [8] with certain modifications. In the nitration of naphthalene-3,6,8-trisulfonic acid the recommended 62% nitric acid was substituted by the equivalent amount of 14.8 M ^{15}N-nitric acid. For the alkali melt 9.64 g ($8.4 \cdot 10^{-3}$ mol) ^{15}N-1-naphthylamine-3,6,8-trisulfonic acid, 2.7 g NaOH and 2.7 ml H_2O were heated in an autoclave for 3 h at 180°. Dilution of the cold melt with 20 ml H_2O and work-up [8] yielded 2.27 g H-acid (76%, nitrite titration, 25% yield with respect to naphthalene) (Rf = 0.1).

^{15}*N-Bisazonaphthalene* **6**. Modifications of procedure [2]: To 0.870 g ($1.93 \cdot 10^{-3}$ mol) ^{15}N-H-acid, 0.020 g Na_2SO_3 and 1.5 ml H_2O, cooled in an ice bath, were added with stirring 0.20 ml 10 M NaOH, 0.212 g Na_2CO_3 and 1.00 g freshly purified tosylchloride. After addition of 0.26 ml 10 M NaOH the mixture was stirred for 2 h at RT., filtered and the filtrate acidified with conc. hydrochloric acid (Congo red). Scratching the sides of the reaction vessel with a glass rod led to precipitation of 0.720 g (40% yield, nitrite titration) ^{15}N-(O-tosyl)-H-acid. Paper chromatography (Rf = 0.5) showed no impurities.

0.720 g ($0.77 \cdot 10^{-3}$ mol) ^{15}*N*-(O-tosyl)-H-acid were dissolved in 5 ml H_2O and 0.20 ml 0.1 M Na_2CO_3, acidified with 0.62 ml conc. hydrochloric acid and diazotized with 7.7 ml 0.1 M $NaNO_2$ in an ice bath. The diazonium salt was coupled by addition of 0.346 g ($0.77 \cdot 10^{-3}$ mol) ^{15}N-H-acid in a solution of 0.90 g Na_2CO_3 in 5 ml H_2O. After acidification with 1 ml conc. hydrochloric acid and addition of 2.0 g NaCl it was again diazotized with 7.7 ml 0.1 M $NaNO_2$. For coupling this solution was mixed with a further 0.346 g ^{15}N-H-acid in 5 ml H_2O, 0.31 ml pyridine and 0.90 g Na_2CO_3. It was then acidified with 1 ml conc. hydrochloric acid and the volume was reduced to 20% of the original. O-Tosylated **6** (0.85 g) was precipitated by addition of 100 ml EtOH (Rf = 0.12).

Detosylation was accomplished by heating with 20 ml H_2O and 0.20 g Na_2CO_3 for 3 h. The solution was concentrated and acidified with 1 ml conc. hydrochloric acid. Precipitation with 3 times the volume of EtOH yielded 0.44 g **6** (Rf = 0.04).

^{15}N-*Trisazonaphthalene* **1**. 0.36 g **6** were diazotized in 10 ml H_2O with 3.3 ml 0.1 M $NaNO_2$ and 1.8 ml 2 M HCl at RT. Excess HNO_2 was destroyed after 1 min with a small amount of sulfamic acid, the solution diluted with 300 ml H_2O and 8 ml 1 M Na_2CO_3 added immediately. After 1 h the solution was concentrated to 15 ml and ^{15}*N*-trisazonaphthalene **1** precipitated with 25 ml EtOH. After dialysis of the inorganic material the yield was 0.117 g (14% with respect to ^{15}*N*-(O-tosyl)-H-acid; Rf = 0.07).

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