107. 11,12-Dihydro-12-hydroxy-tribenzo[*c,g,m*]-1,2,5,6,9,12-hexa-aza-cyclotetradecine; a Neutral Homoaromatic [14]Annulene Macrocyclic Aza Compounds, I[1])

by **P. Skrabal** and **H. Zollinger**

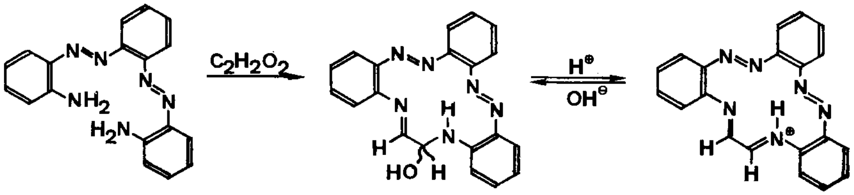
Technisch-Chemisches Laboratorium, Eidgenössische Technische Hochschule Zürich

(25.III. 71)

Summary. The structure of the title compound **2** is supported by spectra and analysis; homoaromaticity is deduced from its NMR. and electronic spectra.

During the last few years, evidence for homoaromaticity has been obtained for several compounds[2]). In this context we describe the properties of the title compound **2**, prepared from 1,2-bis-(2-aminobenzene-azo)-benzene (**1**), in the course of our investigations on conjugation in macrocyclic azo compounds.

After condensation of **1** with glyoxal a yellow product was isolated in 45% yield by thick layer chromatography; its structure was deduced by spectra and analysis.



1 **2** **3**

The mass spectrum showed the molecular ion at *m/e* 338 and an accurate mass measurement led to the formula $C_{20}H_{14}N_6$ (338), which would be in accordance with the macrocyclic compound **3** (unprotonated). Vapour pressure osmometry however, gave molecular weights of 357 and 358 (calc. 356 for **2**). The IR. and NMR. spectra are those required for the carbinolamine **2**[3]).

Carbinolamines are usually very unstable[4]); **2** can be isolated but loses one molecule of H_2O in the mass spectrometer. The IR. spectrum in $CHCl_3$ exhibits a broad band at 3340 cm^{-1} which represents the O–H and N–H stretching frequencies. In the NMR. spectrum (fig.), the integral ratio for the separated signals is 0.9:2:1:11. The proton, represented by the singlet at lowest field, is exchangeable with deuterium (by D_2O) and is therefore the NH proton in the centre of the ring which

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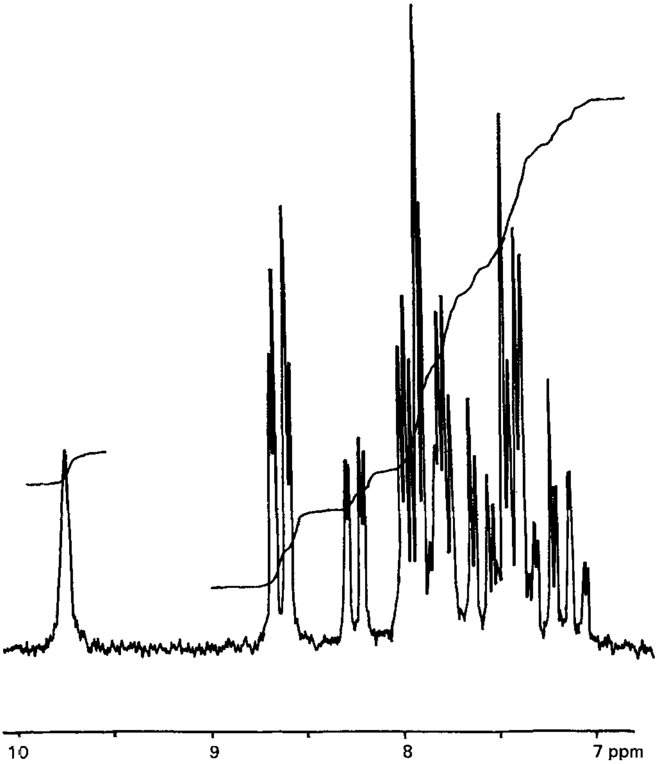
[1]) Preliminary communication. In part presented at the 4. Internationales Farbensymposium in Lindau, May 11–15, 1970 and at the International Symposium on Nonbenzenoid Aromatic Compounds (ISNA) in Sendai, August 24–28, 1970. A full paper is to be submitted to Helv.

[2]) For review see *Winstein* [1].

[3]) A recrystallized sample gave satisfactory elemental analyses.

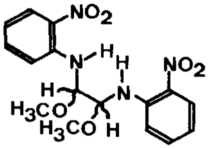
[4]) Recently a macrocyclic carbinolamine ether, stabilized in the form of its Ni complex, has been described [2].

exhibits a strong H bond. No signal for the OH proton is observed due to exchange. The quartet at 8.65 ppm for two protons was proved, by a decoupling experiment, to be an *AB* spectrum with $J_{AB} = 2$ Hz, and is assigned to the nonequivalent CH protons of the carbinolamine and the azomethine groups. A molecular model shows tha the dihedral angle between the C–H bonds is about 55°, which is in agreement with the observed value of the vicinal coupling constant.



^{1}*H-NMR. spectrum of* **2** *in* $CDCl_3$ *(100 MHz)*

The most interesting feature of the spectrum is the absorption of the carbinolamine CH proton at such a low field. Since data for chemical shifts of carbinolamine CH protons are not available, 1,2-dimethoxy-1,2-di-(2-nitrophenyl-amino)-ethane (**4**) was prepared as a model. The CH protons of the $>CHOCH_3$ groups in **4** occur as a doublet centred at 5.13 ppm, which is in the expected region.



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In **2**, one of the carbinolamine groups of the model compound **4** is replaced by a $>C{=}N-$ group which has a certain deshielding effect. Even if one takes into account this effect and since **2** is planar—as seen from molecular models—the difference in the chemical shifts (3.52 ppm) between the carbinolamine CH protons in **2** and **4** can hardly be explained by local anisotropy. The azomethine proton is also expected to absorb at a somewhat higher field. In our opinion the considerable deshielding of these protons in **2** must be explained by a diamagnetic ring current induced in the macrocyclic perimeter; the resonance of the NH proton, at 9.76 ppm supports this interpretation. We have found that NH protons exposed to similar H-bonds absorb about 1 to 2 ppm at lower field; as an inner proton the NH proton in **2** is shielded by the diamagnetic ring current.

The 14 π electron system in **2** consists of six double bonds and two 'lone pair' electrons⁵) on the amino nitrogen atom. The formal conjugation in the perimeter is interrupted by an sp^3-hybridized carbon atom. Therefore, with respect to proton chemical shifts as a criterion for aromaticity, **2** must be regarded as a monohomoaromatic hexa-aza[14]annulene. As far as we know **2** is the first neutral homoaromatic compound; in the past only cationic and anionic homo-aromatic species have been described⁶). We think that homoaromaticity is one explanation of the astonishing stability of the carbinolamine **2**⁷).

The electronic spectra of **1** and **2** compared with that of *Sondheimer*'s[14]annulene are given in the table. It is remarkable that the spectrum of **2** shows a greater resemblance to that of the annulene than to that of the open chain bis-azo compound **1**, in spite of the structural difference between **2** and the [14]annulene (6 heterocyclic aza nitrogens and 3 anellated benzene rings). This may be interpreted as further evidence for strong homoconjugation in the 14 membered perimeter.

Electronic spectra

Compound	λ_{max} (ε)	Solvent
1	313 (21.800), 350 (*sh*, 12.800), 422 (12.100), 475 (*sh*, 8.300)	C_6H_6
[14]annulene[a]	317 (69.000), 333 (35.000), 378 (5.800)	Iso-octane
2	286 (27.800), 300 (*sh*, 24.000), 397 (16.700)	C_6H_6

[a] *F. Sondheimer*, personal communication; see also [6].

Finally we report the dehydration of **2** with acid to give **3**. When a $CDCl_3$ solution of **2**, is acidified, the *AB* spectrum of the vicinal CH protons in **2** is replaced by a singlet at 8.65 ppm representing the azomethine protons in **3**⁷).

We wish to thank PD Dr. *J. Seibl* (ETHZ) for the accurate mass measurement, Dr. *U. Scheidegger* (*Varian AG.*, Zug) for the decoupling experiment, Prof. *J. F. Oth* (ETHZ) for interesting discussions and Prof. *F. Sondheimer* (UCL) for a copy of the spectrum of [14]-annulene. – This work is part of project No. 4430.2 of the *Schweizerischer Nationalfonds zur Förderung der Wissenschaften.*

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5) For discussion of the so called 'lone pair' electrons on azo nitrogen atoms see [3].

6) Recently homoantiaromaticity has been discussed for a neutral derivative of 2,8,10-tridehydro-[17]annulenone [4]. However, the authors did not exclude the possibility that the absorption of the inner protons at low field is due to deshielding by the triple bonds. Homoaromaticity in *cis-cis-cis*-1,4,7-cyclononatriene has only been detected by photoelectron spectroscopy [5].

7) The stabilisation of carbinolamines (*e.g.* **4**), the syntheses of **1**, **2** and **4** as well as the equilibrium **2** $\rightleftharpoons$ **3** will be discussed in forthcoming papers.

BIBLIOGRAPHY

[1] *S. Winstein*, Quart. Rev. *23*, 141 (1969).
[2] *L. T. Taylor, F. L. Urbach & D. H. Busch*, J. Amer. chem. Soc. *91*, 1072 (1969).
[3] *E. Haselbach & E. Heilbronner*, Helv. *53*, 684 (1970).
[4] *J. Griffiths & F. Sondheimer*, J. Amer. chem. Soc. *91*, 7518 (1969).
[5] *P. Bischof, R. Gleiter & E. Heilbronner*, Helv. *53*, 1425 (1970).
[6] *F. Sondheimer*, Proc. Roy. Soc. A *297*, 173 (1967).

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108. A Photoelectron-spectroscopic investigation of the Homoconjugative Interaction between π- and *Walsh*-Orbitals in *endo*- and *exo*-Cyclopropano-norbornene[1],[2]

by **P. Bischof,**[a] **E. Heilbronner,**[a] **H. Prinzbach**[b] and **H. D. Martin**[b]

Physikalisch-Chemisches Institut der Universität Basel[a] und Lehrstuhl für Organische Chemie der Universität Freiburg i. Br.[b]

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Summary. Photoelectron spectra of *endo*- and *exo*-cyclopropano-norbornene (= *endo*- and *exo*-tricyclo[3.2.1.$0^{2,4}$]octa-6-ene) show that a significant homoconjugation exists between the π-orbital of the double bond and the symmetric *Walsh*-e_S-orbital of the cyclopropane ring in the *exo*-isomer, whereas the interaction is negligeable in the *endo*-derivative.

In many cases the characteristics of the photoelectron (PE) spectrum of a molecule largely depend on its configuration and/or conformation.

A typical example is provided by conjugated dienes for which the overlap controlled interaction between the two π-orbitals, π_1 and π_2, leads to an orbital energy split $\varepsilon\,((\pi_1-\pi_2)/\sqrt{2}\,) - \varepsilon\,((\pi_1+\pi_2)/\sqrt{2}\,)$ which is a function of the angle of twist φ between the neighbouring double bonds. As a consequence, the difference $\Delta I_\pi = I_\pi(2) - I_\pi(1)$ between the positions $I_\pi(1)$ and $I_\pi(2)$ (in eV) of the two π-bands in the PE. spectrum of a diene depends also on φ: *e.g.* for 1,3-cyclohexadiene, $\Delta I_\pi = 2.5$ eV; for 1,3-cyclooctadiene, $\Delta I_\pi = 1.3$ eV [2]. Making use of this relationship between ΔI_π and φ *Brundle & Robin* [3] have shown that for hexafluorobutadiene the angle of twist is $\varphi = 50°$.

Similar observations apply to the conjugation of cyclopropyl groups with double bonds; in this case the conjugative interaction of the *Walsh*-orbitals e_S, e_A of the cyclopropyl moiety with the π-orbital of the double bond is at a maximum in compounds for which the relative orientation of the two subsystems corresponds to the so-called bisected conformation: *e.g.* in bullvalene (**1**), in dihydro- and tetrahydro-bullvalene (**2**, **3**) [4], in homofulvene (**4**) [1]. On the other hand, the interaction between the two moieties becomes quite small in molecules in which their orientation corresponds to the perpendicular conformation: *e.g.* homotropylidene (**5**) [4]. As a final example

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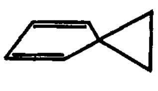
2

3



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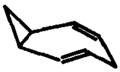

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[1] Part 23 of 'Applications of Photoelectron Spectroscopy'. Part 22: [1].

[2] We use the less cumbersome designation *exo*- or *endo*-cyclopropano-norbornene instead of *exo*- or *endo*-tricyclo[3.2.1.$0^{2,4}$]oct-6-ene.