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[25] *K. Grob,* Helv. *48,* 1362 (1965); *51,* 718 (1968).
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69. The Nature of the Azonium Cation as Evidenced by X-Ray Photoelectron Spectroscopy[1]

by **Edwin Haselbach***), **Anita Henriksson**[2]*), **Andreas Schmelzer***)
and **Hervé Berthou****)

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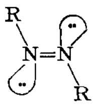
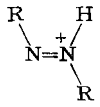
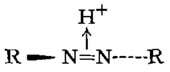
(16. 11. 72)

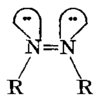
Summary. The question of the classical or non-classical nature of aryl-substituted azonium cations as well as of the pyridazinium cation has been settled by X-ray photoelectron spectroscopy in favour of the classical structure. The relative magnitude of the observed N1s binding energies is reasonably well reproduced on the basis of the theoretically calculated charge structure of these ions. The relative magnitude of the crucial intramolecular potential terms, appearing in the theoretical treatment, is also suggested from PMR.-investigations on protonated azo-compounds. The electronic structure of these species is compared with that implied by commonly accepted classical valence structures and parallels to carbo-cations are drawn. MINDO/2 calculations of the proton affinities of azo-compounds, considering structurally different conjugate acids, also support a classical azonium cation structure. The gas phase basicity of azobenzene is predicted to be higher than that of azomethane.

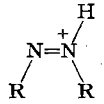
Introduction. – The structure of the azo group in *mono*-protonated *trans*-azobenzene ((I), R = Ph) has been the subject of considerable debate. (For a detailed list of references see [1]). In summary: Based on various indirect experimental observations, some authors favour a *non-classical* structure for the conjugate acid of (I), where the acidic proton is shared in a symmetrical manner by both N-atoms. Two structures have been invoked for this species: the π-complex $(IH^+)^\pi$ [2] and the

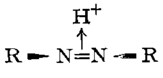

(I)

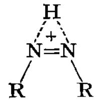

(IH+)


$$\mathrm{R - \overset{H^+}{\overset{\uparrow}{N}}{=}N{-}{-}{-}{-}R}$$
$(IH^+)^\pi$


(II)


(IIH+)


$$\mathrm{R - \overset{H^+}{\overset{\uparrow}{N}}{=}N - R}$$
$(IIH^+)^\pi$


$(IIH^+)^\sigma$

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[1] Electronic structure and physico-chemical properties of azo compounds, part XVI. Part XV: ref. [1].

[2] On leave of absence from the Department of Physical Chemistry, University of Helsinki (Finland).

σ-complex $(IIH^+)^\sigma$ [3], which could also be obtained by protonation of *cis*-azobenzene ((II), R = Ph).

Other workers support the *classical* view that the proton is σ-bonded to one of the N-lone pairs, resulting in the unsymmetrical structure (IH^+) [1] [4].

While it seems fairly certain by now that protonation of (I) or (II) leads to different conjugate acids [5], the question concerning the classical or *non*-classical nature of these still remains in doubt. For example the PMR.-spectra of symmetrically substituted protonated *trans*-azobenzene derivatives indicate a symmetrical structure for the cation, which is also seen for the azo compound in chlorosulfonic acid at −80° or with its fluoroboric or perchloric acid salt in nitromethane or dimethylsulfate [6] (*cf.* Fig. 1). However, this result may be inconclusive in view of the PMR. time scale since a symmetrical structure could correspond to a time average between unsymmetrical ones due to fast proton exchange. This idea is supported

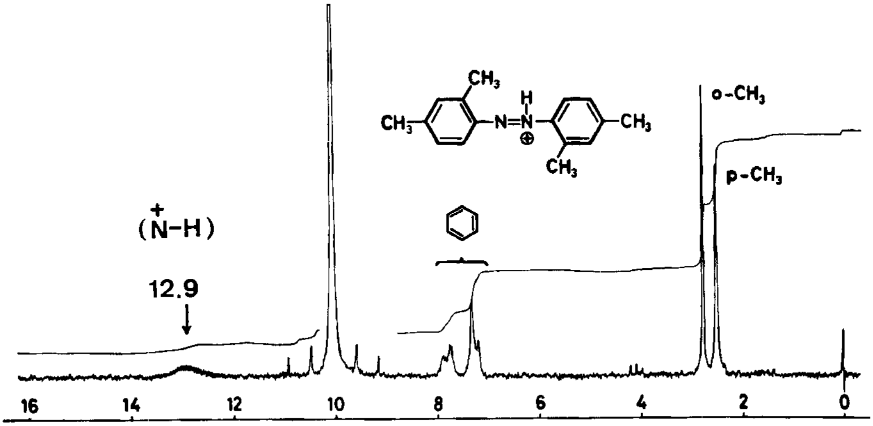


Fig. 1. *PMR.-spectrum of 2,4,2′,4′-tetramethyl azobenzene in $CF_3COOH/HClO_4$* (80%) (1:1 mixture).

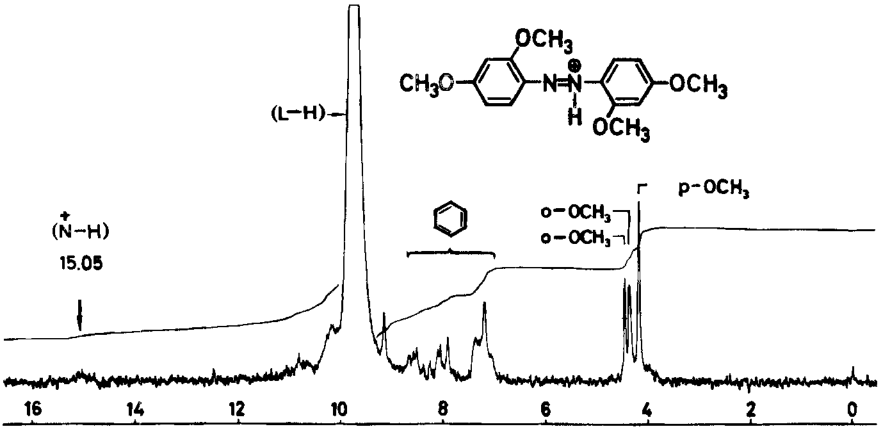


Fig. 2. *PMR.-spectrum of 2,4,2′,4′-tetramethoxy azobenzene in $CF_3COOH/HClO_4$* (80%) (1:1 mixture).

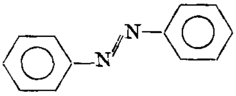
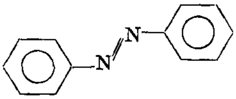
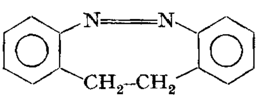
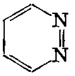
by the result obtained for R = 2,4-dimethoxyphenyl, where a strong N–H····O hydrogen bridge [6] [7] is expected to slow down the exchange process. Here a splitting of the *o*-OCH_3 signals was observed, compatible with the unsymmetrical structure (IH^+) [6] (*cf.* Fig. 2). In addition, an unsymmetrical protonated species was also found in the case of an aliphatic azo compound (R = *t*-butyl) [8].

A much faster experimental technique than PMR. is provided by X-ray photoelectron (ESCA) spectroscopy [9], where the time scale of the measured ionization process is of the order of 10^{-16} sec. Hence definite ionic species are characterized, independent of any equilibration process. It is this feature of the method, which has proved most valuable in studies related to the structure of classical *vs.* *non*-classical carbo-cations [10]. Obviously this technique is most suited for providing a definite answer to the present problem.

ESCA-Experiments and Analysis. – Table 1 lists the N1s binding energies (E_b), obtained for *trans*-azobenzene (I, R = Ph) and its perchloric acid salt [5]. As a representative example for protonated *cis*-azobenzene (II, R = Ph), we have chosen *o,o'*-azoniumdibenzylperchlorate [12]. This latter compound has been shown to exhibit the same electronic spectral features as protonated *cis*-azobenzene [5]. Furthermore, we have studied pyridazinium perchlorate, pyridazine also containing two neighbouring N-lone pairs in a *cis*-configuration. However, the spatial separation between these is larger than in (II), the N=N bond in pyridazine not being an essential double bond.

For (I), E_b(N1s) = 404.5 eV was obtained in good agreement with the value given in [9] (corrected for vacuum level[3])). The linewidth of this band is 2.0 eV[4]). Assuming

Table 1. *N1s binding energies in neutral and protonated azo compounds*

	N1s binding energies	
	center (eV)	peak separation (eV)
	404.5 404.3 [a])	– –
 · $HClO_4$	406.7 406.8 [b])	2.2 1.7 [b])
 · $HClO_4$	406.8	1.6
 · $HClO_4$	407.8	1.6

[a]) Value from ref. [9], corrected for vacuum level [11].

[b]) Values obtained by Dr. *W. Bremser, Varian AG*, Darmstadt, using computer deconvolution.

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[3]) $E_b(N1s) = E_b(N1s)^{rec.} + 290\ eV - E_b(C1s)^{rec}$ [11].

[4]) Linewidth = full width at half height.

the same value to hold also for the N1s-peaks in the protonated species, then the broadness of the bands observed here clearly indicates that two *non*-equivalent N-atoms are present. Graphical deconvolution into two sub-bands using the above mentioned line width yields a satisfactory analysis with the E_b-values[3]) listed in Table 1.

Discussion. – *The classical nature of the protonated azo group.* From Table 1 we deduce a mean difference (ΔE_b) between the two N1s-binding energies in the conjugate acids of $\Delta E_b \approx 2$ eV. Hence these species, which contain the *trans*- or *cis*-azo group, including pyridazine, possess two *non*-equivalent N-atoms. This result can only be rationalized on the basis of the classical structure (IH^+) and (IIH^+) (*vide supra*) for the protonated azo group, where the proton is σ-bonded to one of the N-atoms. We shall later show that this conclusion is in agreement with theoretical calculations about the structure of protonated azo-compounds.

The N1s-ESCA chemical shifts in trans-*azobenzene (I, R = Ph) and its conjugate acid (IH⁺).* From Table 1 we find that protonation of (I) leads to E_b(N1s)-values in (IH^+), which are ~1 eV and ~3 eV ($\Delta E_b \approx 2$ eV) larger than E_b(N1s) in neutral (I). The larger E_b-value in $(IH)^+$ presumably corresponds to the N-atom, which carries the formal charge (N(2)).

$$\mathrm{Ph{-}N_1{=}\overset{\overset{H}{|}}{N}{}^{+}_{2}{-}Ph} \longleftrightarrow \mathrm{Ph{-}\overset{+}{N}_1{-}\overset{\overset{H}{|}}{N}_2{-}Ph}$$

(IH^+) (IH^+)*

However, the 1 eV shift of N(1) might indicate that some charge delocalization occurs, perhaps best represented by a small contribution of the nitrenium valence structure (IH^+)*.

In order to get an impression as to whether the observed ΔE_b-value in (IH^+) is reasonable with respect to the atomic charges on the two N-atoms, we have performed numerical calculations by approximate quantum-chemical procedures, using the CNDO/2- [13] and the MINDO/2-method [14] (Table 2). The general expression for the core electron binding energy of a particular atom A is [9]:

$$E_b(\mathrm{A}) = E_b^0(\mathrm{A}) + \beta_\mathrm{A} q_\mathrm{A} + \sum_{\mathrm{B, B \neq A}} \frac{q_\mathrm{B}}{r_\mathrm{AB}} . \qquad (1)$$

$E_b^0(\mathrm{A})$ is the core electron binding energy of atom A in its zerovalent state relative to the appropriate reference level, q_A is its charge and q_B the charge of an other atom B, situated at a distance r_AB from A. The parameter β_A is the free ionic shift of A, *i.e.* the difference in E_b of A and ionized A^+. ΔE_b in our case is then calculated as

$$\Delta E_b = E_b(\mathrm{N(2)}) - E_b(\mathrm{N(1)}) = \beta_\mathrm{N} (q_{\mathrm{N(2)}} - q_{\mathrm{N(1)}}) + V_{\mathrm{N(2)}} - V_{\mathrm{N(1)}} , \qquad (2)$$

$V_{\mathrm{N(i)}}$ being the intramolecular *Madelung* potentials of the respective N-atoms:

$$V_{\mathrm{N(i)}} = \sum_{\mathrm{B, B \neq N(i)}} \frac{q_\mathrm{B}}{r_{\mathrm{BN(i)}}} \quad (\mathrm{i} = 1, 2) . \qquad (3)$$

For the sake of comparison we have first applied the CNDO/2- and the MINDO/2-method to neutral (I), where $\Delta E_b = 0$. For the charge density q_N the two procedures yield values of -0.065 and -0.21, resp. The CNDO/2-value seems rather small, given that the phenylazo group acts as moderately strong $-$M and $-$I substituent, in both respects comparable with a carbomethoxy group [15]. The MINDO/2 value of -0.21 in (I) can be compared with the N-charge in pyridine of -0.22, found by *non*-empirical calculations [16]. A similarity between these two figures is suggested by HMO perturbation arguments, considering the relevant atom-selfpolarizabilities in the isoconjugate hydrocarbons stilbene (0.478) and benzene (0.398)[5]. The intramolecular potential term V_N in (I) is found by both theoretical methods to be rather small as expected for a neutral aza analog to the alternant hydrocarbon stilbene.

In discussing (IH^+) we shall first consider only the N-charge contribution, *i.e.* the leading term in Equ. (2). From the calculated data in Table 2 it follows that this basis already provides a rational for the overall increase of E_b upon protonation of (I). However, the MINDO/2 difference $\Delta q = q_{N(2)} - q_{N(1)}$ turns out to be unexpectedly small ($+0.027$, Table 2), which together with a reasonable value for the positive free ionic shift of nitrogen $\beta_N = 20.7$ eV/charge unit [9] would account for a splitting $\Delta E_b = E_b(N(2)) - E_b(N(1))$ of the two N-binding energies in (IH^+) of only $+0.56$ eV, *i.e.* about 30% of that observed. The CNDO/2-value for Δq is also small, but appears now with opposite sign ($\Delta q = -0.029$, Table 2). This would imply $E_b(N(2)) < E_b(N(1))$ with $\Delta E_b = -0.60$ eV, a result at variance with the originally proposed sequence, which was based on the consideration of formal charges in the valence structure (IH^+).

Table 2. *Charge densities* (q) *and intramolecular* Madelung *potentials* (V) *for the* $N{=}N$ *group in* trans-*azobenzene* (I, R=Ph) *and the* $N_1{=}\overset{+}{N}_2{-}H_3$ *group in protonated* trans-*azobenzene* (IH^+), *calculated by the CNDO/2- and the MINDO/2-method.*

		$q_{N(1)}$	$q_{N(2)}$	$q_{H(3)}$	$V_{N(1)}$	$V_{N(2)}$
		(charge units)			(eV)	
(I)	CNDO/2	-0.065	-0.065	–	0.43	0.43
	MINDO/2	-0.21	-0.21	–	1.08	1.08
(IH^+)	CNDO/2	0.100	0.071	0.180	5.17	6.78
	MINDO/2	-0.082	-0.055	0.230	5.58	6.56

The situation can drastically be improved by considering the V-terms in Equ. (2), which are now large due to the positive charge in (IH^+) (Table 2). Addition of the MINDO/2-value $\Delta V = V_{N(2)} - V_{N(1)} = 0.98$ eV to the charge contribution yields $\Delta E_b = 1.54$ eV, which is in reasonable agreement with the observed splitting of 2 eV.

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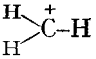
[5] This latter argument rests on the basis that the π-charges obtained in the frame work of a π-electron theory – assuming an unpolarizable σ-skeleton – yield a meaningful guess about the overall charge distribution. It is important to note that this is not always the case if one considers the π-charges obtained by a method, which includes σ-electrons explicitely. In such treatments one finds that the polarity of a system is in many cases already determined by the σ-electrons. The π-electron distribution sometimes works in the opposite direction due to a back donation effect, which decreases total charge separation (electroneutrality principle). An illuminating example of this kind is provided by hydrogen cyanide [17]. Note also that according to the π-charges obtained in the *non*-empirical all-electron calculation cited above [16] each heavy atom in pyridine would be roughly electroneutral, which would result in a negligible dipole moment [18]! For further discussion see [19].

ΔV from CNDO/2 is even larger (1.61 eV) and sufficient to reverse the unexpected E_b-sequence, implied by the N-charge contribution. The final CNDO/2-results is $\Delta E_b = 1$ eV. Note again that both theoretical procedures after inclusion of the V-terms yield $E_b(\mathrm{N(2)}) > E_b(\mathrm{N(1)})$, *i.e.* the sequence suggested by the resonance structure ($\mathrm{IH^+}$).

Analysis of these crucial V-terms reveals that the difference $\Delta V \neq 0$ stems mainly from the fact that N(2) – as compared with N(1) – is situated much nearer to H(3), the latter being the ***most positively charged*** atom in the molecule (Table 2). In support of this, the exchange and/or quadrupole broadened N–H signal in the PMR.-spectrum of Fig. 1 is found at 13 ppm (1H)[6]. In Fig. 2 this downfield shift is seen to be even larger (15 ppm) due to the effect of the N–H···O hydrogen bond. Here, the oxygen lone pairs will repel the N–H bonding electrons, leading to an additional electron deficiency around the H-nucleus.

The charge distribution in the azonium group. Above it was shown that ΔE_b in ($\mathrm{IH^+}$), obtained from ESCA spectra, can only be theoretically reproduced on the basis of the 'potential structure' (not 'charge structure') of the azonium group. Although the two theoretical procedures employed yield somewhat different values for the contributing local charges, they agree in the noteworthy finding that (*i*) $|q_{\mathrm{N(1)}}| \approx |q_{\mathrm{N(2)}}| \leqslant 0.1$ and (*ii*) $q_{\mathrm{H(3)}} \approx 0.2$ (Table 2). The remaining fraction of the $+1$ charge is found to be more or less equally distributed around the two phenyl rings.

These calculated local charges are in apparent disagreement with those implied by the usually drawn valence structure ($\mathrm{IH^+}$), where the protonated N-atom carries the full charge. However, as clearly noted some time ago by *Hoffmann* [21] such an unexpected charge delocalization also occurs in carbenium ions. Recent near *Hartree-Fock* calculations by *Millie & Berthier* [22] for planar methyl cation – usually drawn as  – show that the C-atom carries only 10% of the total charge, the other 90% being located at the H-atoms. Obviously, any deductions about the charge distribution in charged species on the basis of single favorite classical valence structures are unsound. These latter merely reflect the *overall potential* associated with each atom in the molecule.

The high tendency of charge to be delocalized over the whole core of a closed shell molecule (such as ($\mathrm{IH^+}$)) parallels the behaviour of open-shell ions, dealt with in UV.-photoelectron spectroscopy [23]. Here extensive use of *Koopmans'* theorem [24] is made, which implicitely contains the idea that the positive charge in the radical cation is delocalized in a first approximation according to the shape of a canonical SCF-MO. Such MO's are usually strongly delocalized over the whole nuclear frame work[7]. The reasonable success of this approach suggests in turn that the charge

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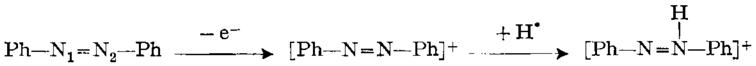
[6] This argument may also explain the low field absorption (14 ppm) of the N-H protons in *di*protonated azobenzene as recently reported by *Olah* [20].

[7] In reality charge delocalization will sometimes be even more pronounced than expected on this basis. Thus the calculated overall charge distribution in the $^2B_2$, $^2B_1$ and $^2A_1$ states of $(\mathrm{CH_2O})^+$ are very similar, although the corresponding singly occupied MO's are quite different in shape [25]. In particular the $^2B_1$-state corresponds to ejection of an electron out of a π-MO, which has zero coefficients at the H-atoms. Nevertheless one calculates a decrease in electron density at these atoms upon $^1A_1 \rightarrow {}^2B_1$ ionization, indicating that the σ-electrons of the C-H bonds are 'attracted' by the positive hole in the π-system.

structure of ions can not be obtained on the basis of single classical valence structures. In this light perhaps a more adequate way to visualize the charge distribution in (IH^+) would be to rewrite the protonation reaction as a two step process of the following form:



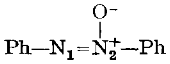
$$\mathrm{Ph{-}N_1{=}N_2{-}Ph} \xrightarrow{-e^-} [\mathrm{Ph{-}N{=}N{-}Ph}]^+ \xrightarrow{+H^\bullet} [\mathrm{Ph{-}N{=}\overset{H}{\overset{|}{N}}{-}Ph}]^+$$

(I) (I^+) (IH^+)

The first step involves ionization of the base (I), the positive charge in the radical cation (I^+) being fairly well delocalized (*vide supra*). In a second step a (neutral) H-atom approaches. Hence, there is no reason for assuming a significant charge localization at N(2) to occur in the process (I^+) ⟶ (IH^+).

In conclusion we wish to emphasize that the insight into the electronic structure of open-shell ions – obtained by photoelectron spectroscopy – should be of considerable value in the discussion of the chemical behaviour of parent closed-shell 'iso-charged' species. Admittedly, it is more common in theoretical chemistry to compare 'iso-electronic' species. In this connection it is interesting to note that the 'iso-electronic' 3-atomic pair of molecules: $^+NH_2$ and CH_2 – although very similar in electronic and molecular structure of the low lying states [27] – behave chemically quite different. As pointed out by *Gassman* [28] the chemistry of nitrenium ions resembles that of carbenium ions. On the other hand there seems to be no indication of nitrenium ions exhibiting carbene-like behaviour [29]. Apparently the presence of the positive charge plays a significant role in their chemistry.

Comment on the ESCA-spectrum of azoxybenzene (III). The most favored classical valence structure of azoxybenzene (III) exhibits the same formal charge situation



$$\mathrm{Ph{-}N_1{=}\overset{O^-}{\overset{|}{N_2^+}}{-}Ph}$$

(III)

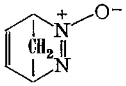
in the azo group as (IH^+). Hence, a comparison of the ESCA-spectrum of (III) with that of (IH^+) may be instructive. The splitting ΔE_b of the two N1s-binding energies in (III) was found to be 4.2 eV [9], *i.e.* about twice as much as that in (IH^+). Furthermore, E_b of the formally uncharged N-atom (N(1)) in (III) is about the same as that in neutral azobenzene (I) [9]. Apparently, the above drawn valence structure of (III) provides a satisfactory rational for both these ESCA results and we may conclude that for estimating local charges, chemical intuition is a more reliable guide in the case of neutral molecules (such as (III)) than for cations (such as (IH^+)).

In agreement with this, CNDO/2 as well as MINDO/2-calculations indicate that $\Delta q = q_{N(2)} - q_{N(1)}$ in (III) is around +0.8–0.9 charge units. The N–O bond in (III) is strongly dipolar with the O-atom carrying about half of a negative charge. This is in line with the considerable dipole moments found for N-oxides and nitrones, which usually range around 3–4 D [30].

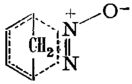
From experimental observations published recently [31], one also might deduce chemical evidence that the N_2-moiety of an azoxy group carries a net positive charge. Thus while the bicyclic system (IV) extrudes N_2 even at low temperatures, the azoxy compound (V) is remarkably stable up to 170° C. The relative rate of N_2 *vs.* N_2O expulsion was found to be in the order of 10^6, while the heat of reaction for both processes was estimated to be roughly the same.

(IV)

(IV)‡



(V)



(V)‡

Both reactions presumably proceed in a concerted fashion and involve the cyclic transition states (IV)‡ and (V)‡, resp., which are topologically analogous to benzene. However, while (IV)‡ possesses the cyclic six-electron system characteristic of *Diels-Alder* transition states, the corresponding system of (V)‡ is expected to be polarized and slightly depopulated due to the semipolar $N^+—O^-$ bond. According to *Dougherty* [32], depopulation of the π-system of benzene by a whole electron, *i.e.* ionization of benzene, results in a decrease of its aromaticity by one order of magnitude. This idea is supported by mass spectrometrical indications that $C_6H_6^+$ exists as an open chain species [33]. Accordingly it is expected that (V)‡ is less aromatic than (IV)‡ and thus – from *Evans'* principle [34] – (V) less reactive than (IV), in line with the experimental facts.

Relative Stabilities of Classical and Non-Classical Azonium Ions. – *Theoretical Procedure.* The MINDO/2 method [14] has been applied with reasonable success to the calculation of heats of formation (ΔHf) of various neutral and charged species [14] [35]. We have now calculated the proton affinities of azomethane (R = Me) and azobenzene (R = Ph), considering the debated structures for the conjugate acid mentioned in the introductory section. We did not minimize the total molecular energy of these species with respect to all geometrical degrees of freedom because of the following reasons: (*i*) for R = Ph, the costs of computation would be prohibitive, (*ii*) all semiempirical procedures of the type used here yield unsatisfactory lengths for bonds between heteroatoms due to the inadequate description of lone pair orbital repulsion [14], and (*iii*) the same procedures yield unrealistic conformations for conjugated systems containing essential single bonds [36]8). We used instead experimentally determined geometrical parameters, where known. For all species involving the *trans*-azomethane heavy atom skeleton, the geometry was taken from [40]. For the corresponding *cis*-structures a larger CNN-angle seems appropriate, which was assumed to be the same as that determined for *cis*-azobenzene [41]. For *trans*-azobenzene, the structural parameters of [38] were employed. The position of the proton in the *non*-classical conjugate acids was optimized within the symmetry restriction imposed by the structural formulae. For the classical structures the approach of the proton to the azo group was assumed to take place in the direction of the N-lone pair of the base. This direction was found by applying the localization procedure of *Edmiston & Ruedenberg* [26] to the MINDO/2 wave functions,

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8) For *trans*-azobenzene (I, R=Ph) the CNDO/2-method yields a preferred conformation, where the C—N=N—C plane is perpendicular to both ring planes [37]. This prediction for the isolated molecule contrasts with the finding that (I) is almost planar in the crystal [38]. It seems also improbable, given that the electronic spectrum of the vapour of (I) is remarkably similar to those obtained from solutions or from the crystal [39].

which yielded localized lone pair orbitals. Their angle with the N=N-bond was thus obtained as: 126° (I, R = Me), 120° (I, R = Ph) and 113° (II, R = Me).

Protonation of trans- *and* cis-*azomethane* ((*I*) *and* (*II*), *R* = *Me*). The calculated value of ΔHf(I) = 56 kcal/mol is in fair agreement with the experimental value ΔHf(I) = 45 kcal/mol [42]. With ΔHf(II) = 62 kcal/mol, the calculated heat for *trans* → *cis* isomerisation ((I) → (II)) is 6 kcal/mol. This value is larger than that found for the isomerisation of 2-butene (≈ 1 kcal/mol [43]), indicating increased non-bonded interaction in the *cis*-azo compound. This can be rationalized by considering the unstrained *trans*-structures, where the values for $r_{N=N}$ and ∢ C–N=N [40] are both considerably smaller than those for $r_{C=C}$ and ∢ C–C=C [44].

Proton addition to (I) or (II) leads with $\Delta Hf(H^+)$ = 366 kcal/mol [45] to the calculated proton affinities (kcal/mol) listed in the figure below. (The structural formulae are given in the introductory section.)

$$\begin{tikzcd}
(IH^+)^\pi & & & (IIH^+)^\pi \\
& (I) \arrow[ul, "185"] \arrow[dl, "216"] \arrow[r, "\text{heat of isomerization}"] \arrow[r, swap, "6\ \text{kcal/mol}"] & (II) \arrow[ur, "184"] \arrow[r, swap, "200"] \arrow[dr, swap, "214"] & (IIH^+)^\sigma \\
(IH^+) & & & (IIH^+)
\end{tikzcd}$$

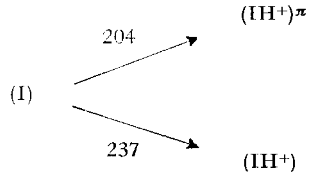
Evidently, by starting with (I), the most favorable conjugate acid is the classical unsymmetrical structure (IH^+), in agreement with the experimental evidence for R = *t*-Bu from PMR. studies [8] and with the ESCA results for R = Ph, discussed previously. Note the excellent agreement between the corresponding calculated proton affinity (216 kcal/mol) and the recently determined gas phase value (212 ± 5 kcal/mol [44]) (which in turn supports the classical conjugate acid structure (IH^+)). Similarly, upon protonation of (II), the classical structure (IIH^+) turns out to be most favoured in agreement with the ESCA results for *o,o'*-azodibenzyl. Since the exothermicity of the processes (I) + H^+ → (IH^+) and (II) + H^+ → (IIH^+) is roughly the same, whereas the isomerisation (I) → (II) is endothermic by 6 kcal/mol, we may conclude that the *trans*-structure (IH^+) is the most stable conjugate acid of azomethane, and that protonation of *trans*-azomethane does not thermodynamically facilitate *trans* → *cis* isomerization.

The π-complex structures $(IH^+)^\pi$, $(IIH^+)^\pi$ lie energetically well above the corresponding classical structures by about 30 kcal/mol. This result is certainly significant, given that semi-empirical procedures (such as the MINDO/2 method [14]) tend to overestimate the stability of bridged as compared with classical open structures. However, it is interesting to note that $(IH^+)^\pi$ corresponds to a minimum on the potential energy surface for $C_2H_7N_2^+$. This was found by displacing the acidic proton by 0.05 Å in various directions from its minimum energy position in $(IH^+)^\pi$. The energies thus obtained are all larger than $\Delta Hf(IH^+)^\pi$, indicating that the isomerization $(IH^+)^\pi$ → (IH^+) needs activation. We did not try to calculate this certainly small and therefore irrelevant isomerization barrier. However, it seems noteworthy to point out this result in view of the presently heavily discussed question of bridged *vs.* classical nature of carbo-cations of *formulae* $C_2H_3^+$, $C_2H_5^+$, $C_3H_7^+$ *etc.* [35] [47]. Note that $(IH^+)^\pi$ contains a three centre-two electron system, which is topologically equivalent to aromatic cyclopropenyl cation. It is perhaps this feature, which renders 'stability' to $(IH^+)^\pi$.

The symmetrical σ-complex $(IIH^+)^\sigma$ is also less favorable than (IIH^+) by about 14 kcal/mol. This statement again involves the comparison between a bridged and a classical structure and seems therefore significant by the same reasons mentioned above for $(IIH^+)^\pi$ *vs.* (IIH^+). However, in this case $(IIH^+)^\sigma$ does not correspond to a minimum on the potential energy surface. Thus abandoning the symmetry restriction imposed on the proton position in $(IIH^+)^\sigma$ leads to a collapse of the species to (IIH^+). The instability of $(IIH^+)^\sigma$ is not unreasonable, given that it involves a three-centre four electron system, equivalent to the *anti*-aromatic cyclopropenyl anion.

Protonation of trans-*azobenzene* ((*I*), *R* = *Ph*). The calculated heat of formation of azobenzene is $\Delta Hf(I) = 121$ kcal/mol. Unfortunately, no experimental gas phase value has been determined yet. $\Delta Hf(I)$ in the crystalline phase is measured as 76.5 kcal/mol [43]. Assuming the heat of sublimation of (I) to be about the same as that of stilbene (20 kcal/mol [43]) or benzalaniline (20.5 kcal/mol [43]), we arrive at an experimental gas phase estimate of $\Delta Hf(I) \approx 97$ kcal/mol. The considerable difference of 24 kcal/mol relative to the theoretical value indicates that the MINDO/2 method is less reliable for calculating heats of formation of larger systems containing heteroatoms than for hydrocarbons of this size [48].

The figure below shows the proton affinities (kcal/mol) calculated for *trans*-azobenzene, considering the classical cation (IH^+) and the π-complex $(IH^+)^\pi$.



Evidently, these results parallel those obtained for *trans*-azomethane. Again the classical conjugate acid (IH^+) is energetically favoured over $(IH^+)^\pi$, in direct agreement with the ESCA-results. Similar calculations as in the case of *trans*-azomethane indicate that $(IH^+)^\pi$ does correspond to a minimum on the potential energy surface. Here it is interesting to note that stable π-complexes of *trans*-azobenzene with metal ligands (instead of H^+) have recently been discovered [49]. Apparently, the back-donation between filled metal orbitals and empty π*-orbitals of (I) suffices to favour the π-complex energetically.

Note that our calculations predict azobenzene to be a much stronger base than azomethane in the gas phase. This is contrary to common knowledge according to which a phenyl group has less capability than a methyl group of stabilizing 'inductively' a positive charge [50]. Here we refer to the important work of *Brauman, Beauchamp, Taft et al.* [51] on gas phase basicities and acidities. These authors showed that commonly accepted substituent effects are in many cases nothing but a manifestation of solvation effects. For isolated molecules in the gas phase, the effect of substituents is sometimes reversed as compared to solution experiments. In general it seems as if the stabilization of a charged species (positive or negative) increases with increasing polarizability of a substituent attached to it. In view of this, the predicted higher 'intrinsic' basicity of azobenzene *vs.* azomethane seems reasonable.

This work is part of project No. SR 2.477.71 of the *Schweizerischer Nationalfonds.*

Helpful discussions with Prof. *C. K. Jørgensen* (Geneva) as well as financial support by *CIBA-GEIGY S.A.* and a gift of computer time by *SANDOZ S.A.* are gratefully acknowledged. We thank Dr. *W. Bremser* of *Varian,* Darmstadt for the measurement of one ESCA spectrum. *A. Schmelzer* would like to thank the *Studienstiftung des Deutschen Volkes* and *A. Henriksson* the *Swiss Government* for a fellowship.

Experimental. – *Trans*-azobenzene and pyridazine are commercially available. *o,o'*-Azodibenzyl was prepared according to [12]. The perchloric acid salts of these bases were obtained using the procedure outlined in [5] and showed satisfactory microanalyses (ratio base/acid = 1). ESCA-spectra were measured with the Varian-IEE-15 instrument at the University of Geneva (for calibration see [11]). PMR.-spectra were recorded on a Varian-A-60 spectrometer, using TMS as internal standard.

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