6. *Substance* **B**: la spectrophotométrie est compatible avec deux structures: celle du tétra-éther-3,5,7,4′ et celle du penta-éther-3,5,7,3′,4′. L'étude des R_M comme les données physico-chimiques concluant à un penta-éther, c'est donc la structure du penta-éther-3,5,7,3′,4′ qu'il faut retenir pour **B**.

7. *Substance* **C**: c'est un di-éther et d'après les R_M, elle ne peut être que le di-éther-7,3′ (tableau 5).

8. *Substance* **D**: d'après l'étude des R_M, c'est un mono-éther, ce que confirme l'étude spectrale d'après laquelle il s'agit du mono-éther-7.

Le tableau 6 résume ces conclusions.

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157. 'Lone pair' Electronic Structure, Conformation and Oxidation Behaviour of Diaziridines

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(22. II. 73)

Summary. Photoelectron spectroscopic investigations indicate that (i) monocyclic diaziridines prefer a *trans*-conformation of the nitrogen-lone pairs, and (ii) the interaction between these is comparable to that exhibited by open-chain analogues, *i.e.* alkyl-substituted hydrazines. The chemical experience concerning the particular ease of —NH—NH— → —N=N— oxidation of diaziridines can therefore not be accounted for by a prevailing unfavorable 'lone pair' interaction. Thermochemical as well as entropy arguments may serve as an explanation. A rather unsatisfactory agreement between predictions from various theoretical procedures and experimental results for the ionization potentials of 'lone pair' MO electrons is noted.

Introduction. – A number of N,N′-unsubstituted cyclic hydrazines exhibit rather short lifetimes in the presence of mild oxidants as compared to acyclic analogues [2]. A rationalization for this fact has been advanced on the basis of a particularly unfavorable lone pair interaction in the cyclic series, using diaziridine as a reference system for the theoretical calculations [3]. While this molecule in principle can exist in the *trans*-(**I**) or the *cis*-(**II**) conformation, only the former has as yet been positively identified by PMR.-spectroscopy in the case of N,N′-dialkylsubstituted derivatives [4].

This finding seems reasonable on steric grounds but such considerations would less apply to *mono*-alkyl N-substituted derivatives and only minimally to diaziridine

itself. Although no PMR.-evidence could be obtained for the presence of the *cis*-form in the latter two cases [4], semiempirical calculations, performed by us using the MINDO/2- [5] and a modified CNDO/2-method [6] [7] do indeed not indicate any
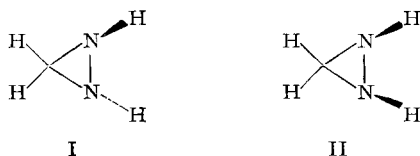
significant energetic preference for **I**. On the other hand, a recent *non*-empirical calculation favours **I** by ∼8 kcal/mol [8]. In order to arrive at more definite conclusions with regard to the two questions indicated above, we measured the photoelectron (PE) spectra of some diaziridine derivatives.

Results and discussion. – In general these PE.-spectra exhibit two bands at lower ionization potentials (IP), well separated from the higher energy band system, which is rather complex for heavily substituted compounds. Experience as well as theoretical calculations (*vide infra*) suggest that these two bands arise from the removal of an electron from one or the other of the 'lone pair' MO's. These MO's are typified by their largest components, being the localized N-lone pairs n_1 and n_2 in a

Table 1. *First two ionization potentials of diaziridines and hydrazines* (all values in eV)

		IP_1	IP_2	Δ
Ia	H\N—CH₃ / H'N—CH₃	9.42	10.03	0.61
Ib	CH₃\N—H / CH₃'N—H	9.90	10.41	0.51
Ic	CH₃\N—CH₃ / CH₃'N—H	9.20	10.05	0.85
Id	CH₃\N—CH₃ / CH₃'N—CH₃	8.94	9.54	0.60
IIa[a])	H\N—CH₃ / H'N—	8.78	10.18	1.40
IIIa[b])	NH_2-NH_2	8.93	9.32	0.39
IIIb[b])	CH_3HN-$NHCH_3$	8.22	8.70	0.48
IIIc[b])	$(CH_3)_2N$-$N(CH_3)_2$	7.93	8.24	0.31

[a])   Sample kindly provided by Professor *E. Schmitz*, Berlin-Adlershof.
[b])   From [11].

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

symmetric (n_+) or antisymmetric (n_-) linear combination. For the present purpose, it is sufficient to restrict the discussion to these 'lone pair' MO's; however, in a future communication [9] further features of diaziridine spectra will be discussed in relationship to those of isoelectronic species already presented in [10].

Table 1 lists the first two vertical IP's observed for various diaziridine compounds in comparison with those for acyclic symmetrical analogues, reported by *Dewar et al.* [11]. The difference Δ is defined as

$$\Delta = \text{IP}\,(n_+) - \text{IP}\,(n_-)\,.$$

From the assumption of predominant 'through space' interaction between n_1 and n_2 [12] as well as from theoretical calculations (*vide infra*) it follows that the quantity Δ is positive for the *cis*- and negative for the *trans*-conformation. (For an analysis of this sign-problem see [12–14]). The important quantity for our purpose is the absolute magnitude of the n_+/n_--splitting. Therefore,

$$\Delta = \text{IP}_2 - \text{IP}_1$$

is listed in Table 1.

1. *The conformation problem.* The symmetrical N, N'-dialkyl compounds **I**a and **I**d, which for reasons indicated above exist in the *trans*-conformation, show $\Delta = 0.6$ eV. This value is close to that observed for **I**b $(\Delta = 0.5$ eV) and much smaller than that for **II**a $(\Delta = 1.4$ eV), where n_1 and n_2 are forced into a *cis*-conformation. We therefore may conclude that **I**b also exists predominantly in the *trans*-conformation, *i.e.* that lone pair interaction [15] is decisive in favoring a *trans* ground state conformation for diaziridines. This is not unexpected since here the dihedral angle Θ_{trans} between n_1 and n_2 lies somewhere in between the most unfavorable values of 0° and 180°, while Θ_{cis} is fixed at 0°. As a direct consequence of this ground state consideration, $\Delta_{cis} \gg \Delta_{trans}$ is observed, due to the better overlap between n_1 and n_2 in the *cis*-conformation. This fact also parallels the oxydation behaviour of such compounds, reported by *Nelsen et al.* [16]. Note, however, that Δ_{cis} is very much smaller than $\Delta_{cis} = 3.55$ eV, found for 3,3-dimethyldiazirine [17]. This can be rationalized on the basis of the corresponding N–N distances which are theoretically calculated for diaziridine (R_{N-N}) as 1.35 Å [3], 1.39 Å [7] and estimated as 1.45 Å [10], while diazirine shows $R_{N=N} = 1.228$ Å [18]. In view of the large difference in Δ_{cis} between **II** and diazirine, the latter (assumed) value for R_{N-N} seems most reasonable. Indeed, the former two values for R_{N-N} were calculated using procedures, which neglect two-centre repulsion terms involving overlap at one centre. They thus underestimate lone-pair dipole-dipole repulsion and consequently yield too short bonds between heteroatoms [5].

Note also the larger value for Δ in **I**c. This is due to the different basis orbital energies for n_1 and n_2 in this molecule, assuming equal interaction between them as in the symmetrical systems **I**a, b, c.
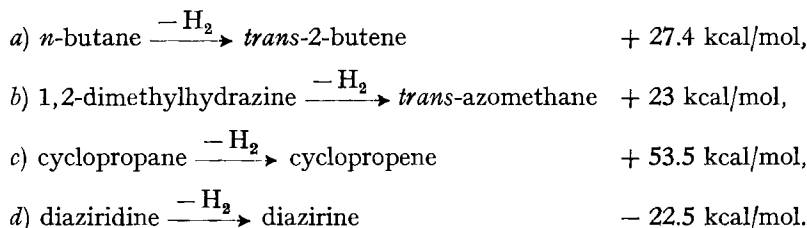
2. *The oxidation problem.* From a comparison between the results (Table 1), obtained for *trans*-diaziridines (**I**) and their acyclic hydrazine analogues (**III**), the following points emerge:

(*i*) The first IP's for **I** are consistently larger than those for **III**. This parallels the behaviour of aziridines when compared with open-chain secondary amines [11]

and might be ascribed to more s-character in the N-lone pairs for the cyclic structures. (A similar argument has been invoked to explain the higher barriers to N-inversion in aziridines [19].) This general trend also agrees with *Nelsen*'s conclusion that 'ring strain apparently causes the oxidation of hydrazines to be more difficult' [16].

(*ii*) The values $\Delta_{trans} \approx 0.6$ eV for **I** and $\Delta \approx 0.4$ eV for **III**[2]) are not significantly different from each other, being in any case much smaller than Δ_{cis}. This is not unexpected since Θ_{trans} in **I** might not be too different from the optimal value $\Theta \approx 90°$, realized in acyclic hydrazines [20].

Apparently, the chemical experience concerning the particular ease of hydrazine → azo oxidation for cyclic precursors can *not* be directly related to an unfavorable N-lone pair situation prevailing in them [3]. For diaziridines, one might point out the extraordinarily high energy of their radical cations which suggests increased reactivity of them, once they are formed. Indeed, *Nelsen* has found irreversible oxidation for systems of this kind [16]. However, an other clue is provided by thermochemical arguments, considering the following heats of dehydrogenation (ΔH)[3]):

a) *n*-butane $\xrightarrow{-H_2}$ *trans*-2-butene   + 27.4 kcal/mol,

b) 1,2-dimethylhydrazine $\xrightarrow{-H_2}$ *trans*-azomethane + 23 kcal/mol,

c) cyclopropane $\xrightarrow{-H_2}$ cyclopropene   + 53.5 kcal/mol,

d) diaziridine $\xrightarrow{-H_2}$ diazirine   − 22.5 kcal/mol.

From $\Delta H(a) \approx \Delta H(b)$ it follows that formation of a C=C or a N=N double bond from the corresponding single bond is about equally endoenergetic. $\Delta H(c)$ has increased, indicating a larger strain in cyclopropene relative to cyclopropane. From the above relationship, one might intuitively predict $\Delta H(c) \approx \Delta H(d)$ and therefore $\Delta H(d) \gg \Delta H(b)$. However, the reverse seems to be the case, the difference $\Delta H(b) - \Delta H(d)$ being about 45 kcal/mol. Note furthermore, that process *d*) is predicted to be exothermic! Unless the errors made in estimating ΔHf (diaziridine) and ΔHf (diazirine) [24] do not add up to 45 kcal/mol, the relative ease of oxidation of diaziridines follows from these thermochemical considerations. However, we admit that we are somewhat surprised by the unexpected outcome of process *d*). It is suggested that the heat of formation of some diaziridine and of the parent diazirine system should be measured. In any case entropy factors might play a rôle, given that the cyclic systems suffer less loss of conformational mobility upon N=N-formation than their open-chain analogues.

3. *Comparison between theoretical and experimental results.* Finally, we shall compare experimental IP's and theoretical predictions based on *Koopman*'s theorem [25] [26] (Table 2). For this purpose an experimental estimate of IP_1 and IP_2 of the parent unsubstituted compounds **I** and **II** is needed, which were the reference systems

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[2]) The HeII-photoelectron spectrum of hydrazine, recently published in [21], also indicates a value $\Delta \approx 0.5$ eV.

[3]) The heats of dehydrogenation (ΔH) were obtained from the corresponding heats of formation (ΔHf) of reactant and product. All values are from [22], except ΔHf (*trans*-azomethane) [23] and the estimated values ΔHf (diaziridine) and ΔHf (diazirine) [24].

for the calculations. Assuming additivity of alkyl group effects to hold, the following relationships were set up:

$$\text{A) } IP_n(I) = IP_n(Ib) + IP_n(Ia) - IP_n(Id);$$

$$\text{B) } IP_n(II) = IP_n(I) + IP_n(IIa) - IP_n(Ia); \; n = 1, 2.$$

Clearly, the second equation is less convincing since (*i*) it compares *cis-* and *trans-* structures, (*ii*) it assumes that the C_4-ring substituent in II a acts inductively comparably to the separate methyl groups at each N-atom in I a, and (*iii*) it uses the already extrapolated data for I. Another way to look at this would be to take for II:

$$\text{C) } IP_{1,2}(II) = \frac{1}{2} \left(IP_1(I) + IP_2(I) \right) \pm \frac{1}{2} \Delta_{cis}.$$

This equation assumes equal basis orbital energies for n_1 and n_2 in I and II and uses the experimental value Δ_{cis} from II a to set up a symmetrical n_+/n_--splitting. Both estimates are presented in Table 2 and it can be seen that they differ from each other

Table 2. *Comparison between experimentally extrapolated and calculated values for the ionization potentials of* trans-(I) *and* cis-(II) *diaziridine* (all values in eV)

	I			II		
	IP(n_+)	IP(n_-)	Δ_{trans}	IP(n_-)	IP(n_+)	Δ_{cis}
MINDO/2[a])	9.80	10.34	0.54	9.93	10.54	0.61
mod. CNDO/2[b])	10.44	11.71	1.27	10.16	11.27	1.11
CNDO-BW[c])	11.45	11.76	0.31	11.5	12.19	0.69
ab-initio[d])	8.92	11.74	2.82	–	–	–
ab-initio[e])	9.77	10.69	0.92	9.41	11.81	2.40
exp. estimate[f])	10.4 (A)	10.9 (A)	0.5 (A)	9.7 (B)	11.1 (B)	1.4 (B)
				9.95 (C)	11.35 (C)	1.4 (C)

[a])   This paper.
[b])   This paper and from [7].
[c])   From [3].
[d])   From [10].
[e])   From [8].
[f])   See text for methods A, B, C.

within tolerable limits. In any case, either of them seems to be more trustworthy than any of the calculations, which give a rather chaotic picture. While the lack of precision in the prediction of absolute IP's could be understood in view of the approximate nature of the theoretical procedures as well as *Koopman*'s theorem[4]), one might expect the calculated values for Δ_{trans} and Δ_{cis}, or at least their ratio to be of some significance. Unfortunately, this is not the case, in particular not for the semiempirical methods. Most worrying is the divergence found for Δ_{trans} by the two 'ab-initio' procedures. Note that Δ_{trans} of [10] is roughly twice as large as experimentally estimated Δ_{cis}! Since 'lone pair' MO's are of more localized nature than

[4])   Note that *Koopmans*' theorem in particular fails for the N_2-molecule [26].

ordinary σ- or π-MO's, they are particularly sensitive to the choice of basis functions, centred around the heteroatoms.

Conclusions. – The present study leads to the following conclusion:

1. Monocyclic diaziridines exhibit the same conformational preference as their acyclic analogues. In both cases, minimization of unfavorable 'lone pair' interaction in the ground state seems to be the driving force.

2. The differential oxidation capacities of cyclic *vs. non-*cyclic hydrazines can not be accounted for by only considering their 'lone pair' electronic structure. Thermo-chemical considerations suggest that the electronic structure as a whole would have to be considered. Moreover, entropy factors may be of importance.

3. Theoretical calculations for systems of even that size – when containing hetero-atoms – yield rather unsatisfactory results. This is particularly true for semiempirical methods where orbital energies as well as total energies do not account for the obser-vations. The different results from the '*ab-initio*' calculations call for attention since these methods are of '*non*-empirical' nature.

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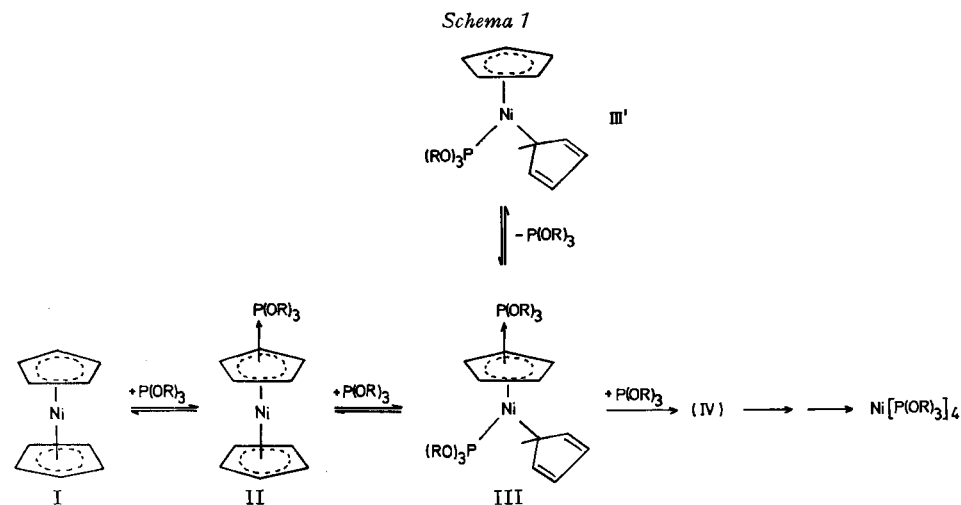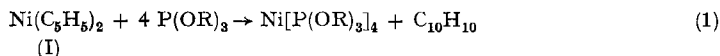# 158. Synthese und Eigenschaften einiger neuer Mono(π-cyclopentadienyl)-Nickel-Komplexe[1])

von **Viktor Harder**[2]) und **Helmut Werner**

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(16. IV. 73)

Summary. During studies on the mechanism of ligand displacement reactions of nickelocene, non-ionic monocyclopentadienylnickel complexes of the type $\pi - C_5H_5Ni[P(OR)_3]X$ with $X = Cl$ and $P(O)(OR)_2$ have been obtained. The new compounds have been characterised by means of their IR., UV., NMR. and Mass spectroscopic data. The phosphonate ligands are bonded with the phosphorus atom to the transition metal.

1. Einleitung. – Nickelocen (I) reagiert mit tertiären Phosphiten unter relativ milden Bedingungen zu den Nickel(O)-Komplexen $Ni[P(OR)_3]_4$ (1).

$$Ni(C_5H_5)_2 + 4\ P(OR)_3 \rightarrow Ni[P(OR)_3]_4 + C_{10}H_{10} \qquad (1)$$
$$\text{(I)}$$

Schema 1