Kurze Mitteilungen

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Rapid scan experiments using a conventional FT-ICR mass spectrometer *

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Abstract

This paper reports results obtained with a home-made FT-ICR spectrometer when it is run in the rapid scan mode described by *McIver*. The ability of the technique for the measurements of wide range mass spectra has been demonstrated.

Fourier transform ion cyclotron resonance spectrometry (FT-ICR) is an efficient technique for the detection of gaseous ions trapped in a magnetic field [1]. A mass spectrum is obtained after processing of the signal corresponding to the image current induced in the ICR cell by the cyclotronic motion of the ions as a response to an excitation by a rf electric field [2]. The excitation frequency is linearly scanned in the limits corresponding to the mass range of interest. For a typical FT-ICR experiment, i.e. when the excitation duration is much shorter than the life time of the ICR signal, the frequency sweep rate is close to 1 MHz ms^{-1}. It is possible to slow down the sweep rate in the range of 1 MHz s^{-1}, which is characteristic for correlation mass spectrometry or rapid scan ICR [3]. In this paper, we would like to present results obtained when our home-made ICR spectrometer is set for correlation spectrometry. Design and capability of our instrument are similar to those described by *Comisarow* and coworkers, which are adequate for the different kind of experiments [4, 5].

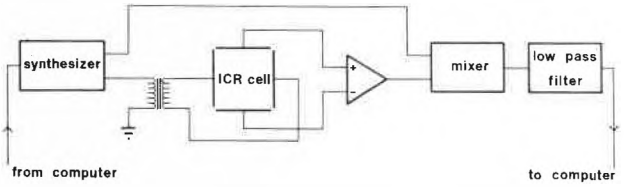

Fig. 1: Configuration of a FT-ICR spectrometer used for rapid scan experiments.

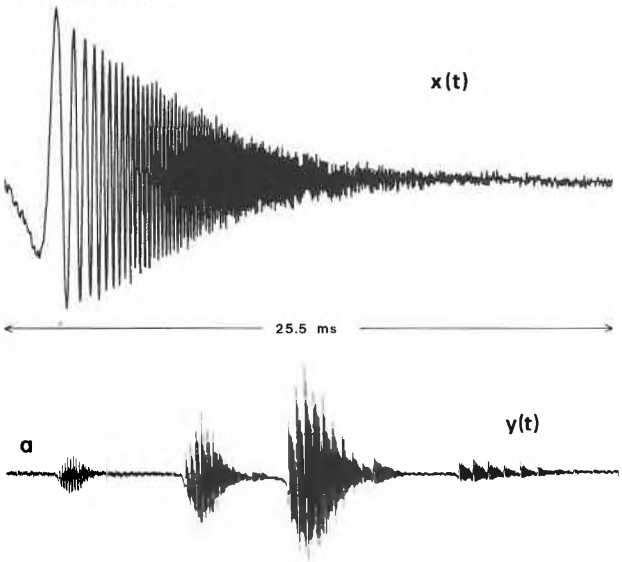

Fig. 2: Typical transient observed at m/z 70 for ions produced in n-heptane (at $4 \cdot 10^{-7}$ Torr) by a pulsed beam of 30 eV electrons. The excitation frequency was scanned at a rate of 1 MHz s^{-1} and the magnetic field strength held constant at 1.5 T.

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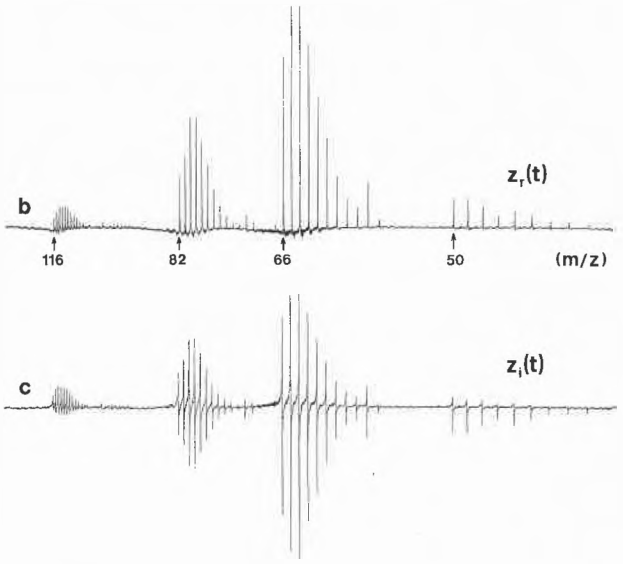

Fig. 3: Spectrum of $C_7H_{16-n}D_n$ (n = 0, 1, ..., 16) measured in the conditions described on Fig. 2.
a) signal given by the output of the low pass filter.
b) result of the cross-correlation of $y(t)$ with $x(t)$.
c) *Hilbert* transform of $z_r(t)$.

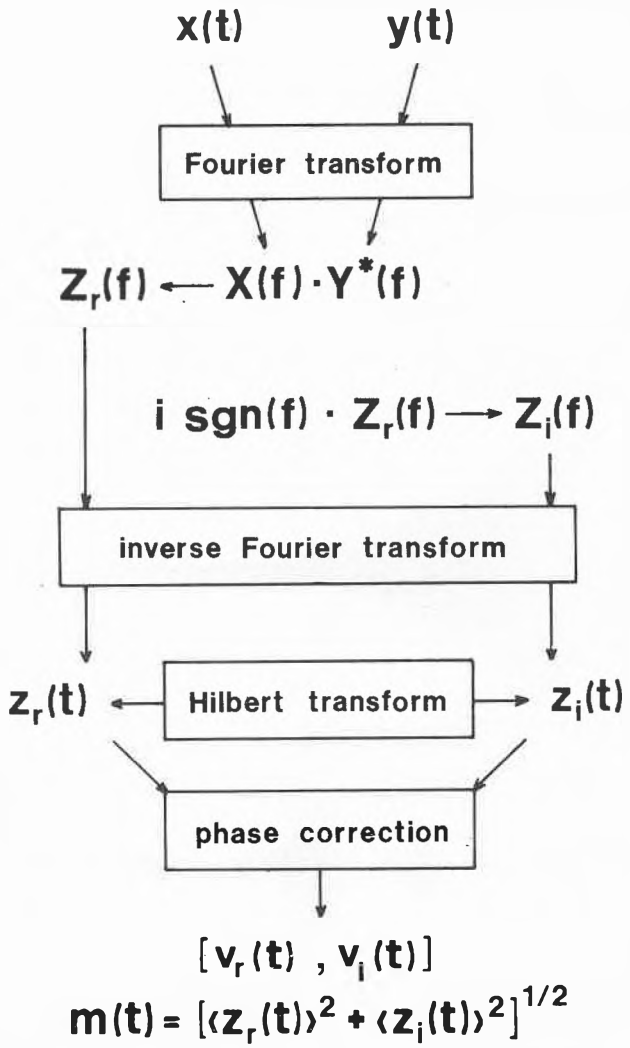

Fig. 4: Flow diagram of the processing.

Fig. 1 shows the configuration of our spectrometer. The ions stored in the ICR cell are excited with the linear frequency sweep generated by a synthesizer. The same signal is given to a mixer in parallel with the preamplified output of the cell. A typical transient observed for a population of ions with the same m/z ratio is shown on Fig. 2. The actual frequency of the signal induced by the ions, i.e. the cyclotronic frequency, isn't visible on Fig. 2 because of the combined action of the mixer and a low pass filter.

The mass spectrum of a mixture of deuterated n-heptanes ($C_7H_{16-n}D_n$, n = 0, 1, ..., 16) has been measured at $4 \cdot 10^{-7}$ Torr following ionization by a pulsed beam of 30 eV electrons. During the experiments, the magnetic field strength was held constant at 1.5 T. The result $y(t)$ (Fig. 3a) is the consequence of the overlap of the signals due to ions with different m/z ratios. The processing described by the flow diagram on Fig. 4 is the way to get a mass spectrum in a more conventional form. In the first step, $z_r(t)$ (Fig. 3b) is obtained after cross-correlation of the signal $y(t)$ with a reference line $x(t)$ measured in the same experimental conditions. The spectrum $z_r(t)$ shows a slight phase shift which appears to be linear with the frequency. This phase shift is more easily revealed on $z_i(t)$ (Fig. 3c) which is the *Hilbert* transform of $z_r(t)$ [6]. During the pro-

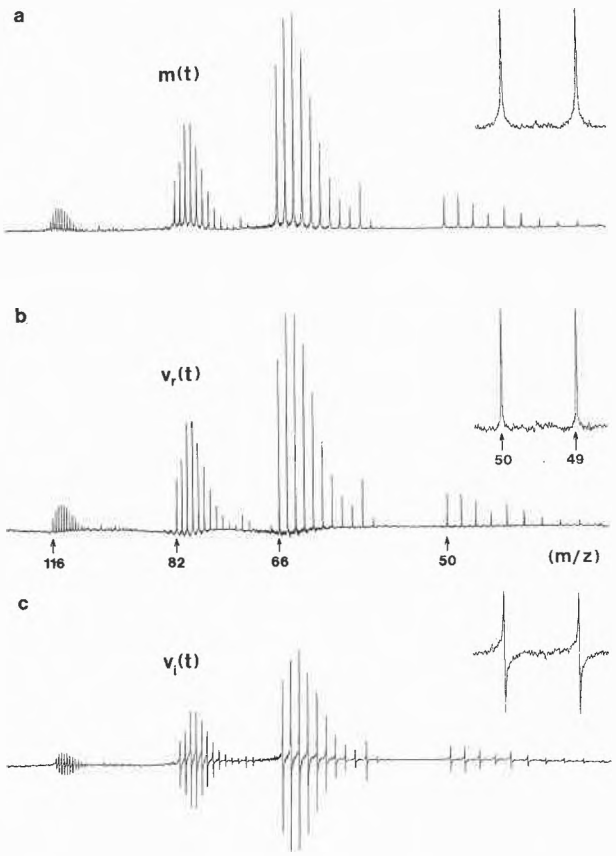

Fig. 5: a) magnitude-mode spectrum calculated from $z_r(t)$ and $z_i(t)$.
b, c) effect of the phase correction routine.

cessing, the cross-correlation is advantageously computed using Fourier transform techniques. It is essential to point out that once the complex conjugate multiplication corresponding to the cross-correlation in the co-domain is done, it is easy to get either the spectrum $z_r(t)$ or its *Hilbert* transform $z_i(t)$. Then $z_r(t)$ and $z_i(t)$ can be used to calculate the magnitude-mode spectrum $m(t)$ (Fig. 5a) or they can be phase corrected with a routine commonly used in FT-NMR. In the last case, $v_r(t)$ and $v_i(t)$ (Fig. 5b and 5c) are obtained with line shapes characteristic for absorption-mode and dispersion-mode spectra. When high mass resolution is needed, it is worthwile to phase correct a spectrum because the peaks are narrower on $v_r(t)$ than on $m(t)$.

In conclusion, we have shown that correlation mass spectrometry is another interesting way to run a conventional FT-ICR spectrometer. A comparison of the different techniques used with this instrument will be presented later [5].

Acknowledgments

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On the Mechanism of Extraction of Uranium(VI) from Nitric Acid Solutions by Di-(2-ethylhexyl)-phosphoric Acid Gels *

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Abstract

The gel-liquid extraction of U(VI) has been investigated at nitric acid concentrations ranging from 0.01 to 10 N using gels prepared by swelling styrene divinyl benzene beads with mixtures of solutions of di-(2-ethylhexyl)-phosphoric acid and nitrobenzene. Extraction at acidities below 5 N HNO_3 seems to be controlled by both a cation-exchange and a solvation mechanism. At higher acidities, a solvation mechanism appears to predominate.

Introduction

The principles of gel-liquid extraction of metal ions have been discussed in a previous publication [1]. The technique simply involves the replacement of the conventional solvent extraction process by a column operation in which the solution of the ion to be separated is passed through a column packed with the extractant after gelatinization. Only few publications [2–8] have appeared in this field. All of these were concerned only with the process application and did not deal with the extraction mechanism.

Investigations [9] have indicated that uranium (VI) can be efficiently extracted from 0.05 N nitric acid solutions by gels prepared by swelling low crosslinked styrene divinylbenzene (SDVB) with di-(2-ethylhexyl)-phosphoric acid (HDEHP) extractant and nitrobenzene diluent. The gel capacity has been found to depend on its HDEHP content. At saturation the molar ratio of sorbed uranium (VI) to the HDEHP content of the gel has been found to be 1:2. The present study has been performed to extend the work to the extraction of U(VI) at different nitric acid concentrations and to acquire some information on the extraction mechanism.

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Experimental

Materials and Reagents

The copolymer (styrene crosslinked with 2% divinylbenzene), the extractant (HDEHP) and the diluent (nitrobenzene) were obtained and purified as mentioned before [1].

General Procedure of Gel Preparation and U(VI) extraction

In general the procedure adopted for gel preparation was similar to that previously described [1]. Gels of different HDEHP content could be prepared by soaking the copolymer in solution mixtures of varying proportions of HDEHP and nitrobenzene. The HDEHP contents of the prepared gels were determined as mentioned elsewhere [9].

The extraction technique consisted in soaking the gel in 20 ml solution of uranium(VI) in nitric acid of the specified concentration. After equilibration, the phases were separated and uranium in the aqueous phase was determined spectrophotometrically by the thoron [10] or the arsenazo III [11] method or polarographically using the catalytic nitrate wave [12]. The distribution coefficient of uranium, D_u, was calculated as follows:

$$D_u = \frac{\text{amount of U(VI)/g dry SDVB}}{\text{amount of U(VI)/ml of aqueous phase after equilibration}}$$

Results and Discussions

As shown from Fig. 1 and 2, the distribution cofficient, D_u, for the gel-liquid extraction of uranium(VI) from

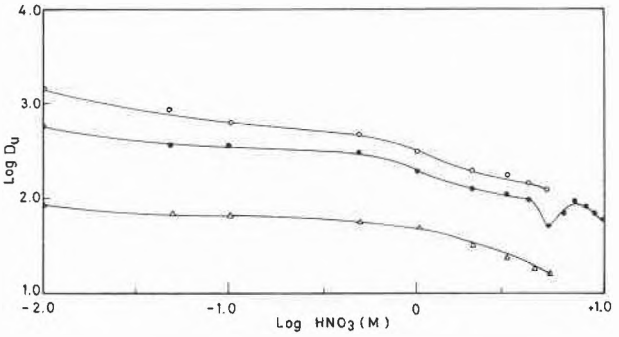

Fig. 1: Extraction of uranium (VI) at different aqueous nitric acid concentrations by gels containing 593 mg HDEHP/g dry SDVB. Initial U (VI) concentration: (○) 0.001 M, (●) 0.01 M, (△) 0.02 M.

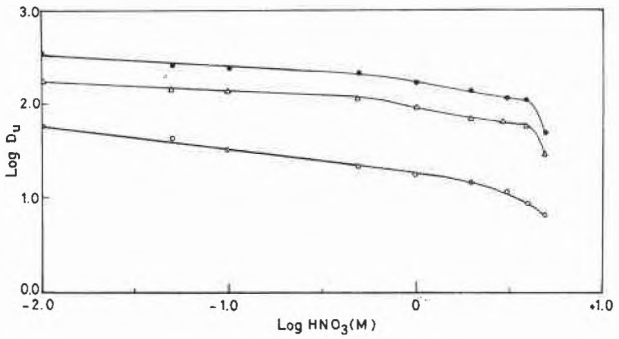

Fig. 2: Extraction of uranium (VI) from aqueous solutions of varying nitric acid concentrations by gels of different HDEHP content.
(●) 496 mg HDEHP/g dry SDVB, 0.01 M U (VI),
(○) 496 mg HDEHP/g dry SDVB, 0.02 M U (VI),
(△) 373 mg HDEHP/g dry SDVB, 0.01 M U (VI).

nitric acid solutions decreases with increasing acidity at acid concentrations below 5 M. Above this acidity the partition coefficient increases to reach a maximum at about 7 M HNO_3 and then decreases with further increase of acidity. Analogous extraction patterns were observed [13–19] in the liquid-liquid extraction of U (VI) with HDEHP and other dialkylphosphoric acid solvents. For such systems, it has been found that at low acidities, uranium (VI) is extracted by a cation-exchange reaction and at higher acidities by a solvation mechanism similar to that found with non-ionic reagents as, for example, tributyl phosphate (TBP) [19, 20], which is usually described by the reversible equation:

$$UO_{2(aq)}^{++} + 2NO_{3(aq)}^{-} + 2TBP_{(org)} \rightleftarrows UO_2(NO_3)_2 \cdot 2TBP_{(org)} \quad (1)$$

The equilibrium constant, K_1, for this reaction may be expressed by the relationship:

$$K_1 = \frac{UO_2(NO_3)_2 \cdot 2TBP_{(org)}}{UO_{2(aq)}^{++}\, NO_{3(aq)}^{-2}\, TBP_{(org)}^{2}} \quad (2)$$

In extraction with dialkyl phosphoric acids solutions in organic diluents according to reaction (1), the equation becomes complicated due to the dimerization of the extractant. In gel-liquid extraction the situation is even more complicated due to the lack of data concerning the state of the extractant in the gel. However, assuming that HDEHP, in the gel, is aggregated, n being the aggregation number, and that at high acidities the gel-liquid extraction of uranium (VI) takes place by the combination of m molecules of HDEHP polymer with each UO_2^{++} by a reaction similar to that observed with TBP, then the reaction may be represented by the equation:

$$UO_{2(aq)}^{++} + 2NO_{3(aq)}^{-} + m(HX)_n \rightleftarrows UO_2(NO_3)_2\,(HX)_{mn(org)} \quad (3)$$

The equilibrium constant K_3 of the reaction may be expressed as follows:

$$K_3 = \frac{UO_2(NO_3)_2 \cdot (HX)_{mn(org)}}{(UO_{2(aq)}^{++})\,(NO_{3(aq)}^{-})\left(\frac{C_d - mnC_u}{n}\right)^m} \quad (4)$$

where
C_d refers to the total HDEHP concentration expressed as monomer,
C_u the organic phase $UO_2(NO_3)_2$,
$(C_d - mnC_u)$ refers to the free or uncomplexed $(HX)_n$, and the parentheses refer to mmole fraction.
Since the distribution coefficient relationship is expressed as

$$D_u = UO_{2(org)}^{++} / UO_{2(aq)}^{++} \quad (5)$$

the following relationship can be obtained for equation (5),

$$\text{Log } n^m D_u = \log K_4 + 2 \log NO_3^- + m \log (C_d - mnC_u) \quad (6)$$

At very low uranium (VI) loadings, the quantity C_u would be very small in comparison to C_d and it may therefore be neglected. As shown from Fig. 3, at minute uranium loadings ($C_u/C_d \sim 1/1000$), log D_u versus log HDEHP is a straight line with a slope very

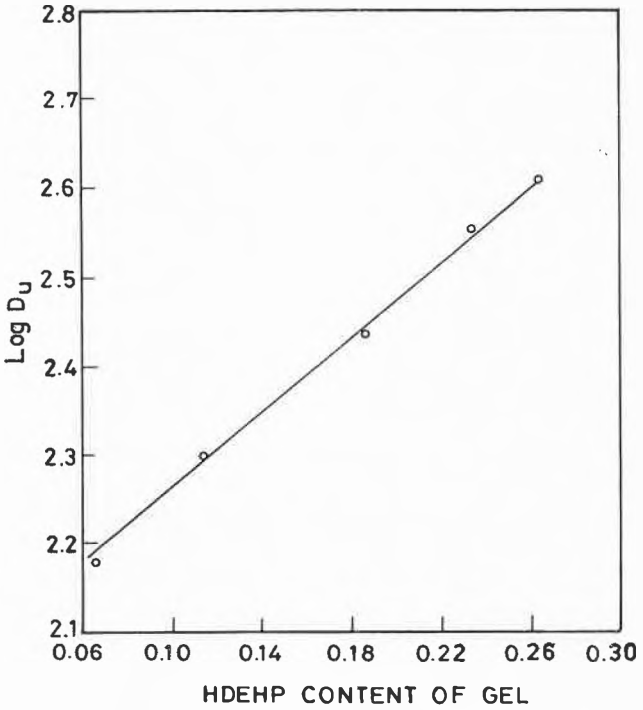

Fig. 3: Variation of D_u with the HDEHP content of the gel at initial concentrations of 6.88 N HNO_3 and 10^{-4} M uranium (VI).

close to 2. Assuming that at this low uranium loading the value mnC_u is negligible then the equation of the gel-liquid extraction of uranium(VI) at high acid concentrations may be:

$$UO_2^{++} + 2\,NO_3^- + 2\,(HX)_n \rightleftarrows UO_2(NO_3)_2 \cdot 2\,(HX)_n \qquad (7)$$

Equation (7) leads to the following relationship:

$$\log n^2 D_u + \log K_7 + 2 \log (C_d - 2n\,C_u) \qquad (8)$$

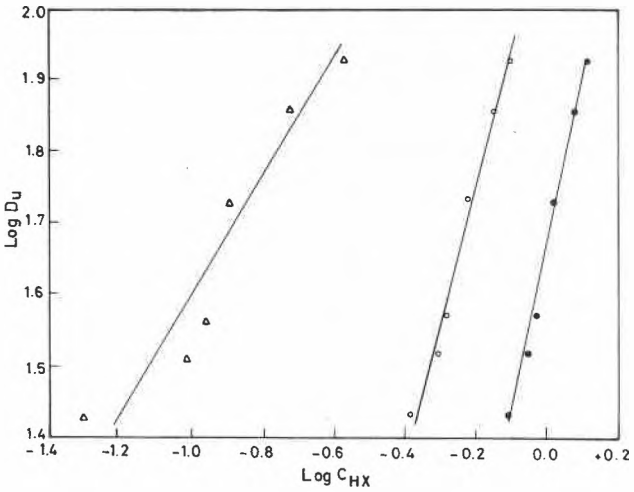

Fig. 4: Dependence of D_u upon the HDEHP content (C_{HX}) of gels at 6.88 M HNO_3 and 0.015 M U(VI).
C_{HX}: (△) $C_d - 6C_u$, (○) $C_d - 4C_u$, (●) $C_d - 2C_u$.

As shown from Fig. 4, where the values of log D_u were plotted versus log $(C_d - 2nC_u)$ assuming different values (1, 2 or 3) for n, a straight line with a slope of about 2 was obtained when the value 2 was substituted for n. This indicates that HDEHP in the gel is most probably dimeric.

If it is assumed that at low acidities the decrease in the distribution coefficient with the increase of HNO_3 concentration is governed by an ion exchange reaction and that $(HDEHP)_{org}$ is dimerized (as was found above), the extraction of UO_2^{++} from aqueous nitric acid solutions can be represented by equation (9) which was found to apply in the liquid-liquid extraction of uranium(VI) from perchloric [21] or sulphuric [22, 23] acid solutions:

$$UO_{2(aq)}^{++} + 2\,(HX)_{2(org)} \rightleftarrows UO_2X_4H_{2(org)} + 2\,H_{(aq)}^+ \qquad (9)$$

From equation (9) the following relationship can be deduced [17, 23]:

$$\log 4 D_u = \log K_9 + 2 \log (C_d - 4\,C_u)/C_H \qquad (10)$$

However, when values of log D_u were plotted versus log $(C_d - 4C_u)/H$ (Fig. 5) at constant HNO_3 concentrations ranging from 0.05 to 0.5 N, it was found that equation (9) is not satisfied.

If it is assumed that, under our conditions, a polymeric uranium-HDEHP complex is formed, in addition to the reaction presented by equation (9), as it was found in the liquid-liquid extraction of uranium(VI) from nitric [19] or sulphuric [23] acid solutions of low acidity, viz.,

$$UO_2X_4H_{2(org)} + UO_{2(aq)}^{++} + (HX)_{2(org)} \rightleftarrows (UO_2)X_6H_{2(org)} + 2\,H^+ \qquad (11)$$

the overall reaction will be:

$$2\,UO_{2(aq)}^{++} + 3\,(HX)_{2(org)} \rightleftarrows (UO_2)_2X_6H_{2(org)} + 4\,H_{(aq)}^+ \qquad (12)$$

and the following relation [18] should hold:

$$\log 4 D_u = \log K_{12} + 2 \log (C_d - 2C_u)/C_H \qquad (13)$$

When values of log D_u were plotted versus log $(C_d - 2C_u)/C_H$ at varying HDEHP concentrations and constant acidity of 0.05, 0.08, 0.1 and 0.5 N (Fig. 5), it was found that equation (13) is apparently more or less satisfied, the slopes of the lines being about 1.7. Thus, it seems that at low nitric acid concentrations, a polymeric UO_2^{++}-HDEHP complex is formed and extraction according to equation (12) occurs.

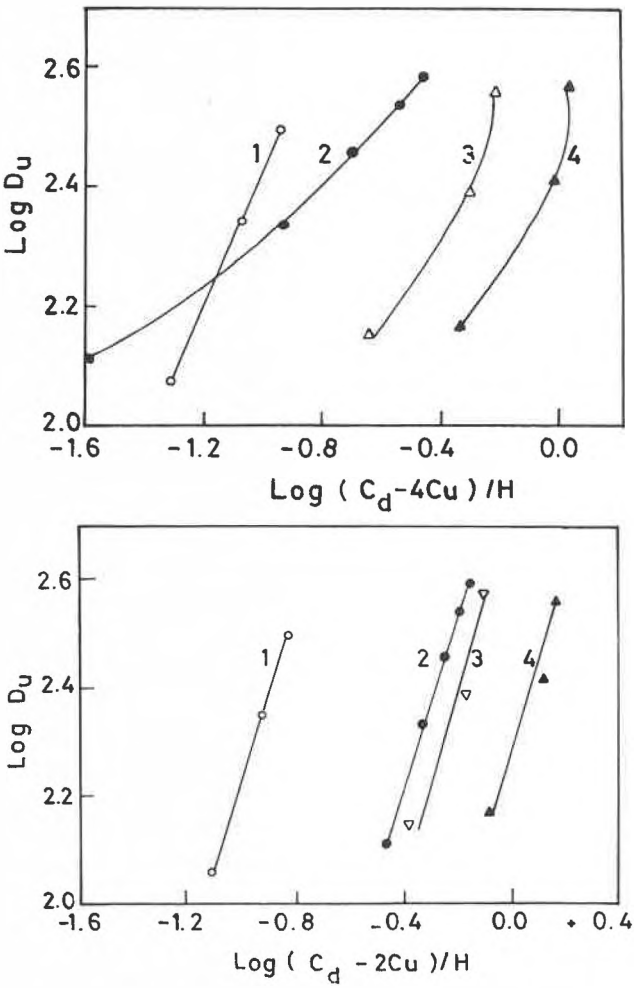

Fig. 5: Log D_u versus log $(C_d - 4C_u)/H$ or log $(C_d - 2C_u)/H$ at different levels (0.05 N–0.5 N) of HNO_3 and of U(VI).

Curve no.:	1	2	3	4
HNO_3, N:	0.5	0.09	0.1	0.05
U(VI), M:	0.01	0.015	0.01	0.01

In order to investigate the hydrogen ion dependency

of the partition coefficient, values of log D_u were plotted versus log $(C_d - 2C_u)/C_H$ at constant concentration of HDEHP in the gel and various aqueous acidity but it was found that equation (12) is not satisfied in the acid range examined (0.05–0.5 N HNO_3) since D_u tended to show positive deviation from straight line and the slopes of the lines were too low. However, it is obvious that the non-satisfaction of equations (9) or (12), which involves the liberation of two hydrogen ions for each UO_2^{++} ion, cannot be attributed to either trimerization (or higher polymerization) or monomerization of the extractant in the gel phase.

Since results in the present work were all obtained at *p*H values < 2, the deviation of our results from equation (9) or (12) cannot be attributed to the formation of polymeric uranyl species [24] in the aqueous phase. This deviation may therefore imply that gel-liquid extraction of U (VI) from dilute nitric acid solutions is not totally governed by an ion-exchange reaction.

A reaction similar to that predominating at high acidities (equation 7) probably takes place besides the cation-exchange reaction. Thus, on increasing the aqueous acidity both the hydrogen and nitrate ions concentrations increase. The increase of the hydrogen ion concentration causes a decrease in the magnitude of D_u while the increase of nitrate ion seems to increase it and consequently the obtained partition coefficient values would be the resultant of the contra-effects of hydrogen and nitrate ions.

Assuming that the HDEHP is present in the gel in the dimerized form, then equation (14) may be proposed for the extraction of UO_2^{++} at low acidity in addition to the ion-exchange equations (equation 9 and 12):

$$UO_2^{++} + 2\,NO_3^- + (HX)_2 \rightleftarrows UO_2(NO_3)_2H_2X_2 \qquad (14)$$

Equation (14) leads to the relationship:

$$\log 2\,D_u = \log K_{14} + \log (C_d - 2C_u) \qquad (15)$$

The above relationship is similar to that obtained (equation 13) assuming a polymeric cation exchange reaction. This implies that if log D_u is plotted versus log $(C_d - 2C_u)$, a straight line with a slope = 1 is obtained if the extraction takes place according to equation (15). If it takes place according to equation (12) then log D_u versus log $(C_d - 2C_u)$ should be a straight line whose slope is 2. Experimentally, the obtained slope is about 1.7, i.e., in between 1 and 2 which may indicate that the extraction, in the present case, takes place according to equation (12) and (15).

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Gas Phase Protonation of Enamines *

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Abstract

The proton affinities and ionization energies of several enamines and of the corresponding saturated amines have been determined. From these data the hydrogen affinities of the molecular cations were calculated. The results yield energetic and structural insight into the protonation reaction of enamines in the gas phase.

Recent theoretical work [2] on the reactivity of enamines towards H^+ prompts us to report our experiments in the gas phase, pertinent to this question [3].

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The data collected in the accompanying table allow the following remarks and conclusions:

1. The difference in the gas phase proton affinities (PA)

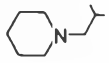
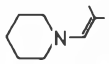
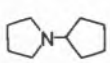
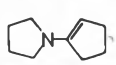
$$\Delta PA(2,1) = PA(2) - PA(1) < 0$$

may be rationalized on the grounds that sp^2-hybridized carbon is more electronegative than sp^3-C. Note, that in **2** the n- and π-basis functions are orthogonal. In line with this are the relative hydrogen affinities (HA)

$$\Delta HA(2^{\cdot+}, 1^{\cdot+}) = HA(2^{\cdot+}) - HA(1^{\cdot+}) > 0;$$

i.e. the radical electron in the HOMO of ground state $2^{\cdot+}$ – with respect to $1^{\cdot+}$ – is more apt to localize itself at the N-atom and to form the bond with a H-atom in the conjugate acid $2H^{+}$. Likewise, the positive

Table 1:

		PA[a] [kcal mol^{-1}]	I[b] [kcal mol^{-1}]	$\Delta\varepsilon_{n,\pi}$ [eV]	HA[c] [kcal mol^{-1}]
1		231.5 231.4[d]	185.6[d]	–	103.5
2		228.7 228.5[d]	194.6 194.6[e]	0.96	109.7
3		230.2	190.0	–	106.6
4		233.6	172.7	2.66	92.7
5		232.3	188.2[f]	–	106.9
6		230.7[d]	182.9[f],[g]	1.37	100.0
7		232.5	184.5	–	103.4
8		238.7[d]	163.7[h]	2.56	88.8

[a] Determined by ion cyclotron resonance spectroscopy (ICR); values relative to PA (tri-n-propylamine) = 233.4 kcal · mol^{-1} [4]. The ICR spectrometer built at the EPF-Lausanne uses a flat four-section cell operated in the trapped ion mode [5].
[b] First vertical ionization energy.
[c] HA = I + PA − I($H^{\cdot}$). Note that the heat capacity $C_p(e^-)$ properly cancels out if I($H^{\cdot}$) = 313.6 kcal mol^{-1} is used.
[d] Ref. 4.
[e] *Brown, R.S.:* Can. J. Chem. *54* (1976) 1521.
[f] Ref. 6.
[g] *Itoh, T., Kaneda, K., Watanabe, I., Ikeda, W.* and *Teranishi, S.:* Chemistry Letters *1976*, 227.
[h] *Houk, K.N.*, and *Domelsmith, L.N.:* Tetrahedron Letters *1977*, 1981.

charge in 2^+ finds less opportunity to be stabilized by C–C hyperconjugation throughout the C-skeleton.

2. Removal of the orthogonality between the N-lone pair and the C=C π-bond basis function in **2** and allowing their interaction as realized (and manifested by the increase in the orbital splitting $\Delta\varepsilon_{n,\pi}$) in the enamines of **4**, **6** and **8** does not lead to a coherent picture with respect to basicity: While ΔPA (**4**, **3**) and ΔPA (**8**, **7**) are positive, ΔPA (**6**, **5**) < 0. Note also that the absolute values $|\Delta PA|$ are rather small. We conclude that the relative basicity of an enamine and of the corresponding saturated amine depends strongly on the system in question (vide infra).

3. A more uniform picture evolves from the pattern of ionization energies (I): ΔI (**2**, **1**) > 0, but $\Delta I < 0$ for the other pairs. These values clearly demonstrate the absence or presence, respectively, of enamine resonance in the radical cation ground states. The same conclusion can be drawn from the ΔHA-data: $\Delta HA(2^{\dagger}, 1^{\dagger}) > 0$, while ΔHA for the other couples < 0. Judging from molecular models **6** is the least conjugating system for steric reasons; as a result $|\Delta I(6,5)|$, $\Delta\varepsilon_{n,\pi}(6)$ and $|\Delta HA(6^{\dagger}, 5^{\dagger})|$ have the smallest values. This steric feature appears ultimately also responsible for $\Delta PA(6,5) < 0$ (c.f. 2.).

4. With respect to the question of C- vs. N-protonation it appears safest to concentrate on **4**. This compound is (except for an additional CH_3-group) a formal hydrogenation product of **2**. The experience of photoelectron spectroscopy suggests that substituent effects on the reactive centres are very similar in **2** and **4**; these two bases are thus ideal for the purpose of disclosing the features of enamine resonance. We note in passing that from photoelectron spectroscopy **2** exhibits $\varepsilon(n) = -8.44$ eV/$\varepsilon(\pi) = -9.40$ eV, while **4** has $\varepsilon(n - \lambda\pi) = -7.49$ eV/$\varepsilon(\pi + \lambda n) = -10.15$ eV [6]. Hence, allowing for resonance interaction in **4**, the ensuing displacement of orbital energies occurs under essential preservation of the centre of gravity, its slight upward shift possibly indicating that overlap cannot be fully neglected. This result once more demonstrates that **2** and **4** differ essentially only with respect to enamine resonance.

Assuming protonation of **4** at the N-atom, the corresponding PA (i.e. PA_N) would be about equal to that of **2** (which undoubtedly protonates at the N-atom), reduced by the resonance energy (RE) of **4**. For the latter we take RE $\sim$ 4 kcal mol^{-1} as established from equilibration studies between enamines and isomeric homo-enamines [7]. We thus arrive at an estimated PA_N (**4**) of $\sim$224.5 kcal mol^{-1}, which is well below the experimental figure. Note also that PA_N (**2**) is larger than estimated PA_N (**4**), but PA_N (**2**) < PA (**4**) experimentally. From this it follows that **4**, under thermodynamical control, most probably is protonated at C_β, and that therefore the difference in PA's between C- and N-protonation of **4** amounts to about $\Delta PA_{C,N}$ (**4**) $\sim$ 9 kcal mol^{-1}.

We shall not apply the above treatment to the other enamines, for which a model system equivalent to **2** is lacking. One may, however, envisage that for enamines with equally delocalized π-system as present in **4**, $\Delta PA_{C,N}$ is also positive. Steric inhibition of resonance may, on the other hand, well lead to a sign inversion, the ideal example for this being **2**. Judging by the arguments put forward under 2., **6** may already belong to that class. It follows that a similar generalization with respect to the magnitude of $|\Delta PA_{C,N}|$ is impossible, as the latter depends strongly on the system in question. Nevertheless, we note a striking similarity between our result for $\Delta PA_{C,N}$ (**4**) and earlier experimental [8] and theoretical [9] estimates for $\Delta PA_{C,N}$ of vinylamine, the simplest member of the enamine class of compounds.

5. An estimate of the enamine radical cation resonance energy may be obtained from the ionization energies of **1** to **4**. Assuming ΔI (**2**, **1**) as due purely to the change in C–C hyperconjugation, the ionization energy of a hypothetical nonconjugating system, i.e. $\mathbf{4}_{nc}$, may be calculated as

$$I(\mathbf{4}_{nc}) = I(\mathbf{3}) + \Delta I(\mathbf{2},\mathbf{1}).$$

Hence, the stabilization of $\mathbf{4}^{\dagger}$ due to n–π conjugation with respect to $\mathbf{4}_{nc}^{\dagger}$ (i.e. the resonance energy of $\mathbf{4}^{\dagger}$, RE) is given as

$$RE(\mathbf{4}^{\dagger}) = I(\mathbf{4}_{nc}) - I(\mathbf{4}) = 26 \text{ kcal mol}^{-1}.$$

Another way of arriving at that quantity is to consider just the frontier orbital energy change in passing from **2** to **4**. This leads to RE ($\mathbf{4}^{\dagger}$) = 0.95 eV $\triangleq$ 22 kcal mol^{-1}, in close agreement with the result of the former approach. An essential prerequisite for the latter is the aforementioned fact that the energy shifts between the highest two orbitals of **2** and **4**, by virtue of the near preservation of their centre of gravity, are directly related to the absence or presence of enamine resonance in the respective radical cations. The results for RE ($\mathbf{4}^{\dagger}$) indicate a strong stabilizing delocalization of the positive charge in the ion, in agreement with the finding, that enamines are readily oxidized with rather weak oxidants [10]. A complete account of the present results will be given in a full paper.

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Palladiumkomplexe mit porphinoidem Ligandsystem *,**

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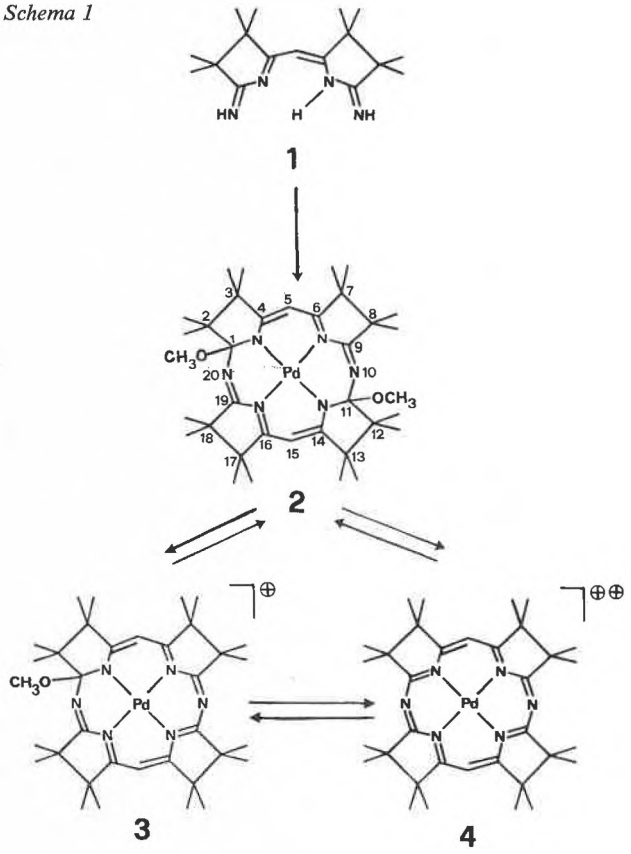
Abstract

In the presence of palladium (II) salts the bicyclic amidine **1** forms diazaporphinpalladium complexes by cyclocondenation. Depending on the reaction conditions the 1,11-dimethoxy complex **2**, the 1-methoxy complex **3** or the annulene complex **4** are obtained. **2**, **3** and **4** can be interconverted by reversible addition and elimination reactions.

Komplexe mit makrocyclischem Ligandsystem, die als Zentralatom Kobalt auf der formalen Oxydationsstufe (I) (d^8) enthalten, reagieren ausgehend vom Metall bezüglich elektrophilen Kohlenstoffverbindungen als sogenannte Supernucleophile [2]. Beispiele dafür sind Vitamin-B_{12s} [3], Cobaloxime [4], Kobalt(I)phthalocyanine [5] und die Vitamin-B_{12}-Modellverbindung 1-Hydroxy-[8H-HDP]kobalt(I) [6]. Die isoelektronischen Metallkomplexe mit Nickel(II) (d^8) als Zentralatom hingegen sind demgegenüber bedeutend weniger reaktiv und der Angriff eines Carbeniumions findet nicht am Zentralatom, sondern an einem Stickstoffatom des Liganden statt [7]. Eigene Rechnungen basierend auf einem «extended *Hückel* Modell» [8] (SCCC-MO mit zusätzlich quadratischer Ladungsiteration am Zentralatom) zeigen, dass für Vitamin B_{12s} und 1-Hydroxy-[8H-HDP]kobalt(I) die obersten besetzten Orbitale vorwiegend Metallcharakter haben, während in entsprechenden Nickel(II)-Komplexen das höchste besetzte Orbital ein reines Ligand-π-Orbital ist und energetisch tiefer liegt [9].

Grundsätzlich ist zu erwarten, dass sich Palladium-Komplexe ähnlich wie Nickel-Komplexe verhalten. Es stellt sich dabei jedoch die Frage, ob in Palladiumkomplexen mit porphinoidem Ligandsystem gewisse Orbitale mit Metallcharakter genügend angehoben sind, so dass das Zentralatom bezüglich elektrophilen Kohlenstoffverbindungen als Nucleophil reagieren kann. Um dieser Frage nachzugehen, wurden die Komplexe **2**, **3** und **4** synthetisiert.

Schema 1



Als Ausgangsmaterial diente das vinyloge Amidin **1**, welches aus Aceton über Tetramethylbernsteinsäuredinitril in vier Stufen und hoher Ausbeute bequem zugänglich ist [10]. Wie beim Aufbau der entsprechenden Nickel- [11] und Kobaltkomplexe [1] erfolgte die Cyclisierung nach Komplexierung zweier Liganden **1** an einem gemeinsamen Pd(II)-Zentralatom durch Kondensation unter Abspaltung von Ammoniak. Zur präparativen Darstellung von **2** wurde **1** und frisch bereitetes Diammonium-tetrachloropalladat im molaren Verhältnis 2:1 erst in Methanol gekocht und anschliessend mit Natriummethanolat umgesetzt, wobei sich cis-1,11-Dimethoxy[10H-HDP]palladium(II)

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(**2**) in über 96 % Ausbeute bildete. Durch Behandlung mit wasserfreien Säuren sind daraus durch stufenweise Elimination der Methoxyreste das Monomethoxy-Derivat **3** und der Annulen-Komplex **4** leicht zugänglich. Umgekehrt lässt sich aus **4** durch Addition von Methanolatanionen ebenfalls stufenweise wiederum **3** und **2** bereiten. Wie bei den entsprechenden Nickelkomplexen [11] verlaufen diese Additions- und Eliminierungsreaktionen mit praktisch quantitativer Ausbeute.

Experimenteller Teil

Allgemeine Arbeitsbedingungen siehe [10].

cis[1,11-Dimethoxy-2,2,3,3,7,7,8,8,12,12,13,13,17,17,18,18-hexadecamethyl-10,20-diaza-decahydroporphinato] palladium (II) (**2**) *(abgekürzt: cis-1,11-Dimethoxy[10H-HDP] palladium)*

In 160 ml Methanol wurden 8,0 g (45 mMol) Palladiumdichlorid und 4,8 g Ammoniumchlorid unter Rühren bei RT. während 16 Std. zu $(NH_4)_2$ $PdCl_4$ umgesetzt. Nach Zugabe von 25,9 g (90 mMol) **1** [10], gelöst in 100 ml Methanol, wurde unter Argon 5 Std. unter Rückfluss gekocht. In das klare, gelbe Reaktionsgemisch wurde eine Lösung von 24,3 g (450 mMol) Natriummethanolat in 200 ml Methanol innert 30 Min. zugetropft und anschliessend 40 Std. gekocht. Nach Abkühlen auf RT. wurden langsam 230 ml Wasser zugegeben, 15 Min. gerührt, das hellgelbe Kristallisat durch Filtration durch eine Glasfilternutsche abgetrennt, 3mal mit wenig Methanol/Wasser 2:1 und 1mal mit Methanol gewaschen und 72 Std. bei 25°/0,01 Torr getrocknet; 30,8 g **2** (96,5 %). Zur Analyse wurde 3mal aus Methylenchlorid/Methanol 1:1 umkristallisiert und 16 Std. bei 50°/0,01 Torr getrocknet.

$C_{36}H_{56}N_6O_2Pd$ Ber.: C 60,76 H 7,93 N 11,81 %
Gef.: C 60,71 H 8,08 N 11,78 %

UV./VIS. (EtOH, log ε): 408(4,09), 390Sch(4,00), 303(4,00), 258Sch(4,03), 245(4,09). – IR ($CHCl_3$): 2970s, 1670m, 1580s, 1565m, 1511s, 1475m, 1430s, 1375s, 1290s, 1152s. – ^{1}H-NMR ($CDCl_3$): 0,77 bis 1,30 Signalhaufen mit einzelnen Linien bei 0,77, 1,06, 1,10, 1,14, 1,30 (total 48H, 16 CH_3-); 3,44(s, 6H, 2CH_3O-); 4,97(s, 2H, olefinische H). – MS (Direkteinlass, 50° Pd = 106) 710(M^+, 3,5), *679*(M^+-OCH_3, 100), 648(M^+-2OCH_3, 75), 633(66), 618(40), 603(25), 588(30), 573(15), 558(23), 543(10), 528(17), 513(5).

[1-Methoxy-2,2,3,3,7,7,8,8,12,12,13,13,17,17,18,18-hexadecamethyl-10,20-diaza-octahydroporphinato] palladium-trifluormethylsulfonat (**3**) *(abgekürzt: 1-Methoxy[8H-HDP] palladium-trifluormethylsulfonat).*

In 20 ml Methanol wurden 1,42 g (2,0 mMol) **2** aufgeschlämmt und 1,75 ml (2,0 mMol) 1,14 N Trifluormethansulfonsäure in Methanol zugegeben. Nach 16 Std. Kochen am Rückfluss wurde filtriert und das klare Filtrat eingedampft. Nach 24 Std. Trocknen bei 25°/0,01 Torr verblieben 1,66 g **3** (100 %) als gelbes Kristallisat. Zur Analyse wurde aus CCl_4/CH_3OH umkristallisiert und 24 Std. bei 60°/0,01 Torr getrocknet. UV./VIS. ($CHCl_3$), 423 (3,89), 393(3,95), 373(3,94), 356(3,92), 308(4,41), 260(4,15), 241(4,15); – IR. ($CHCl_3$), 2960m, 1710w, 1700w, 1548m, 1494s, 1270s, 1150s, 1140s, 1107s. – ^{1}H-NMR ($CDCl_3$) 0,92 bis 1,42 Signalhaufen mit einzelnen Linien bei 0,92, 1,17, 1,22, 1,30, 1,39, 1,49 (total 48H, 16CH_3-); 3,25(s, 3H, CH_3O-), 6,07(s, 1H); 6,35(s, 1H).

[2,2,3,3,7,7,8,8,12,12,13,13,17,17,18,18-Hexadecamethyl-10,20-diaza-hexahydroprophin] palladium-bis-tetrafluoroborat (**4**) *(abgekürzt: [6H-HDP] palladium-bis-tetrafluoroborat)*

In 70 ml abs. Methylenchlorid wurden unter Argon 13,3 g (18,7 mMol) **2** aufgenommen und mit einer Lösung von 23 g (121 m Mol) Triäthyloxoniumtetrafluoroborat in 100 ml abs. Methylenchlorid versetzt. Erst wurde 30 Min. am Rückfluss gekocht und anschliessend 150 ml Methylenchlorid abdestilliert, wobei sich aus der Lösung violette Kristalle auszuscheiden begannen. Nach 2 Std. Stehen bei RT. wurde unter Argon filtriert und das Kristallisat 3mal mit 10 ml abs. Methylenchlorid gewaschen und 16 Std. bei 25°/0,01 Torr getrocknet. 13,2 g **4** (86 %).

$C_{34}H_{50}B_2F_8N_6Pd$ Ber.: C 49,61 H 6,12 N 10,21 %
Gef.: C 49,50 H 6,17 N 10,16 %

UV./VIS. ($CHCl_3$ enthaltend 5 % Triäthyloxoniumtetrafluoroborat) 452(4,05), 427(4,01), 335(4,36), 294Sch(3,97), 253(3,23), 242(3,23). – ^{1}H-NMR (CH_3NO_2) 1,33(s, 24H, 8CH_3-), 1,40(s, 24H, 8CH_3-), 6,37(s, 2H, olefinische H).

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