175. The UV.-Spectrum and the Photochemical Properties of 1-Ethoxycarbonylimino-pyridinium Ylide[1]

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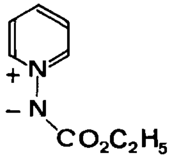
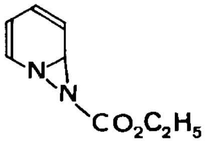
Summary. The UV. spectrum of 1-ethoxycarbonylimino-pyridinium ylide **1** has been measured using the stretched film technique. From a *Pariser-Parr-Pople* model the first two bands can be assigned to $\pi^* \leftarrow \pi$ transitions. The photorearrangement of **1** leading to the diazepine **3** is discussed.

When 1-ethoxycarbonylimino-pyridinium ylide (**1**) is irradiated by UV.-light it isomerizes quantitatively to 1-ethoxycarbonyl-1,2-diazepine (**3**) [1] [2]. The norcaradiene-like diaziridine (**2**) has been postulated as an intermediate, which could result from a photo-induced concerted electrocyclic ring closure of the aromatic 1,3-dipolar species **1**. Rapid valence tautomerization of the intermediate should then lead to the photoproduct **3**.



1



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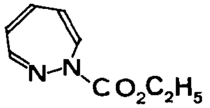

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In order to interpret the electronic spectrum of **1** (Fig. 1) we have measured the dichroism of the ylide **1**, oriented in a stretched polyvinyl alcohol film. If the carbonyl

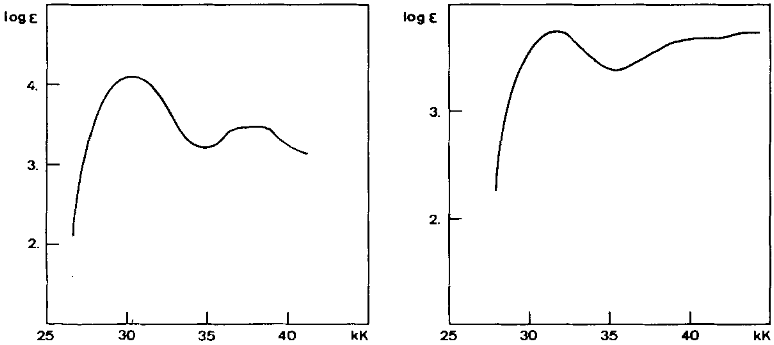

Fig. 1. *Electronic spectrum of* **1** *in chloroform* (left) *and ethanol* (right)

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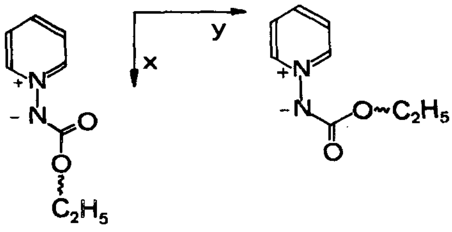
[1] Part 4 of 'Photochemical syntheses of 1,2-Diazepines.' Part 3: [2], Part 5: [9].

[2] Basel.

[3] Mulhouse.

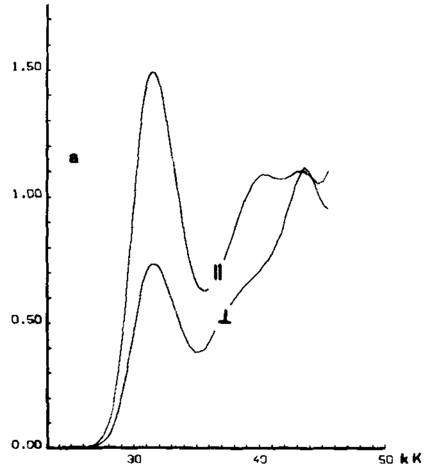
group is assumed to be coplanar with the aromatic ring, only two important conformations **1A** and **1B** have to be taken into consideration.



1A **1B**

Dreiding models indicate that in conformation **1B** the extensions along the x- and y-directions are about equal, whereas in conformation **1A** the extension along the x-direction is about twice as great as along the y-direction. In view of the high observed dichroism it seems reasonable to assume that **1** exists in conformation **1A** with the long axis of the molecule nearly parallel to the N-N-bond.

Unambiguous assignment of the polarization direction from the experimental curves by the method developed by *Eggers* [3] requires at least C_{2v} molecular symmetry. Since **1** has at most C_s symmetry our results are only approximate in character.



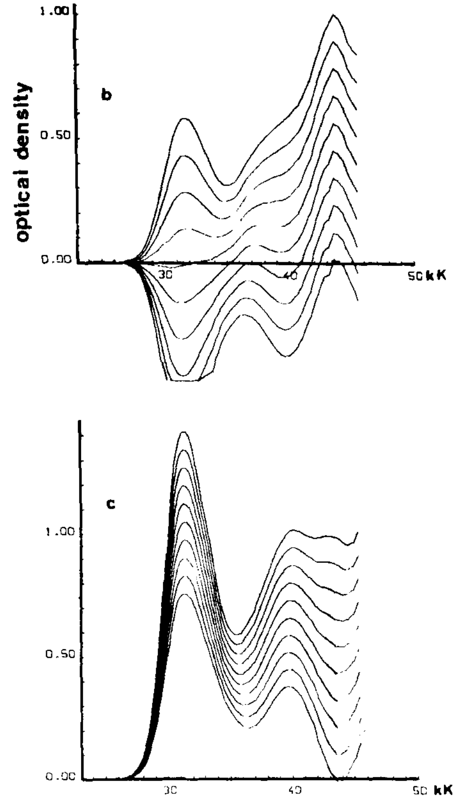


Fig. 2. *Electronic spectrum of* **1** *in stretched polyvinylalcoholfilm*

The spectra reproduced in **a** are obtained with light parallel (||) and perpendicular (⊥) to the stretching direction. The reduction [3] of the two components is shown in **b** for the perpendicular component and in **c** for the parallel one

Since it is possible to reduce [3] the perpendicular component of the first band but not the parallel component (see fig. 2b and 2c) we infer that the vector of the first transition is approximately parallel to the long axis of the molecule in conformation **1A**.

In the same way we deduce that the transitions at 31.6 and 40.0 kK are polarized approximately parallel and those at 37.0 and 43.6 kK are polarized approximately perpendicular to the long axis of the molecule. In order to rationalize the spectra of **1** and the photo-isomerization **1** → **3** we have carried out LCAO-SCF-CI calculations of the *Pariser-Parr-Pople* type. Since the exact structure of **1** is not known, we assumed the following structural parameters for conformation **1A**: 1.4 Å for all interatomic distances except for C–N (amide) = 1.34 Å and C=O = 1.24 Å. All angles were assumed to be 120°. The parameters used for the PPP calculation were: $U_{\dot{C}} = 11.42$ eV, $U_{\dot{N}} = 14.12$ eV, $U_{\dot{O}} = 14.0$ eV, $U_{\ddot{N}} = 19.9$ eV, $U_{\ddot{O}} = 30.4$ eV, $\gamma_{\dot{C}\dot{C}} = 10.84$ eV, $\gamma_{\dot{N}\dot{N}} = 12.30$ eV, $\gamma_{\dot{O}\dot{O}} = 11.30$ eV, $\gamma_{\ddot{O}\ddot{O}} = 22.5$ eV, $\gamma_{\ddot{N}\ddot{N}} = 11.50$ eV. All β-values were taken to be $\beta = -2.318$ eV except for $\beta_{\dot{N}-\ddot{N}} = -1.2$ eV. For the calculation of the two-center electronic repulsion integrals $\gamma_{\mu\nu}$ we used the *Mataga-Nishimoto* relation [4]. In the CI treatment we considered only singly excited configurations. The result of a calculation obtained under these conditions is shown in fig. 3. The theoretical predictions concerning the energies, relative intensities and polarization directions agree quite well with the experimental results.

Our model predicts three $\pi^* \leftarrow \pi$ bands between 39 and 45 kK, but the experimental spectra (see Fig. 2) do not permit an unambiguous correlation with the calculated results for this part of the spectrum. We did not pursue this point since only the first two bands are of importance in this context.

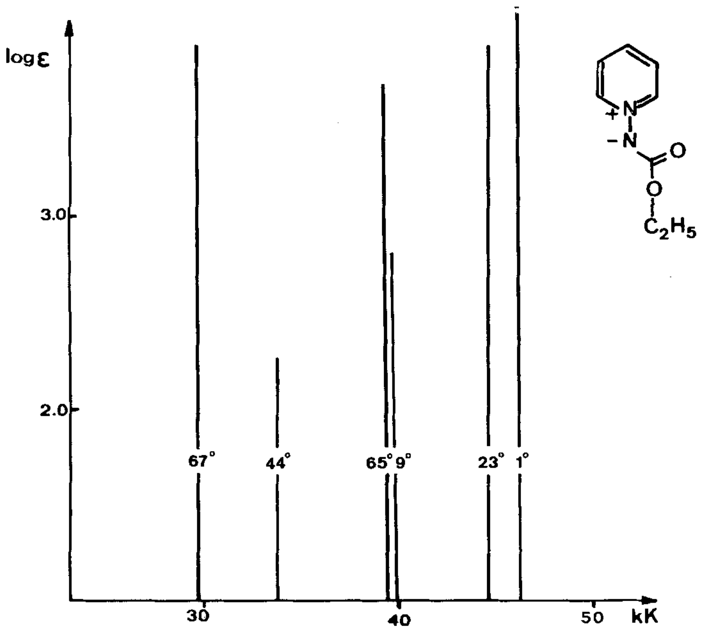


Fig. 3. *Electronic transitions ($\pi^* \leftarrow \pi$) calculated for* **1** *using a PPP model*
The numbers in degrees indicate the angle between the transition moment and the y axis

In Fig. 4a are shown schematically the highest occupied (π_1) and the two lowest unoccupied (π^*_{-1}, π^*_{-2}) MO's of pyridine-N-oxide derived from an extended *Hückel* [5] calculation (EHMO). Recently [6] the photochemistry of pyridine-N-oxide type molecules has been interpreted by taking only the π^*_{-1} level into account. Promoting an electron from π_1 to π^*_{-1} increases the π-bond order between oxygen and the *o*-carbon, and hence isomerization leading to an oxaziridine is understandable. On this basis, as seen from Fig. 4b, the first transition should be parallel and the second perpendicular to the N—O axis. However, measurements by *Seibold, Wagnière & Labhart* [7] show that this sequence is reversed *i.e.* the first band is perpendicular and the second band parallel to the N—O axis. In contrast, a LCAO-SCF-CI calculation of the PPP type [7] [8] does account for this experimental sequence of the transitions (Fig. 4c). The essential point is that the sequence of states is determined by the interaction of configurations resulting from $\pi^*_{-2} \leftarrow \pi_1$ (85%) and $\pi^*_{-1} \leftarrow \pi_2$ (15%) with the result that the first band is polarized perpendicular to the N—O axis. The lowest singlet state (S_1) is essentially a mixture of the configurations mentioned above while, according to a first-order treatment, the second excited singlet state (S_2) is well described by the configuration $\pi^*_{-1} \leftarrow \pi_1$.

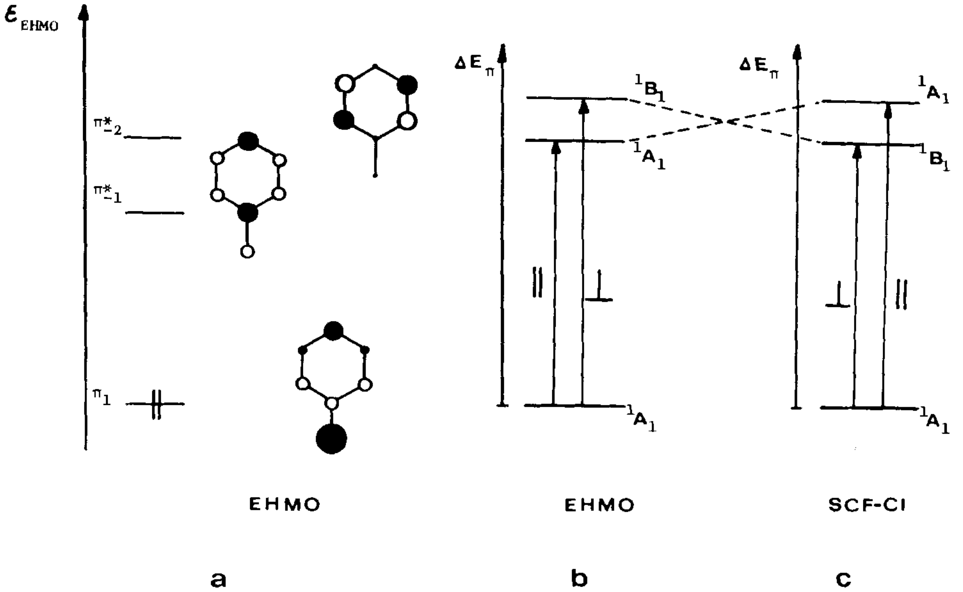


Fig. 4. a) *Schematic representation of the highest occupied and the two lowest unoccupied MO's of pyridine-N-oxide derived from an EHT-model*
b) *Corresponding state diagram to the EHMO-scheme in 4a*
c) *State diagram according to a PPP-calculation*

Experiments carried out so far suggest that the photoreaction **1** → **3** proceeds *via* the first excited singlet state (S_1) [9]. In Fig. 5 are shown the highest occupied MO(π_1) and the lowest vacant MO's (π^*_{-1}, π^*_{-2}) of **1**. The vertical arrows symbolize the first two electronic transitions as predicted by the EHMO and PPP calculation. In this case both models lead to results that are qualitatively similar. Since the lowest excited singlet corresponds essentially to the $\pi^*_{-1} \leftarrow \pi_1$ transition we can discuss the electrocyclic ring closure to **2** in terms of bond-order changes associated with occupation of π^*_{-1}.

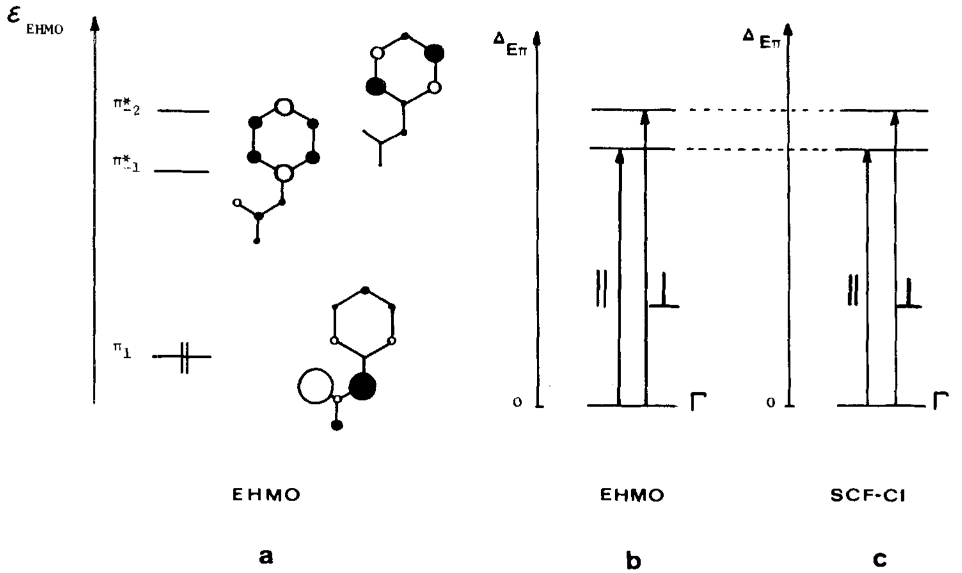


Fig. 5. a) *Schematic representation of the highest occupied and the two lowest unoccupied MO's of* **1** *derived from an EHT-model*

b) *Corresponding state diagram to the EHMO-scheme in 5a*

c) *State diagram according to a PPP-calculation*

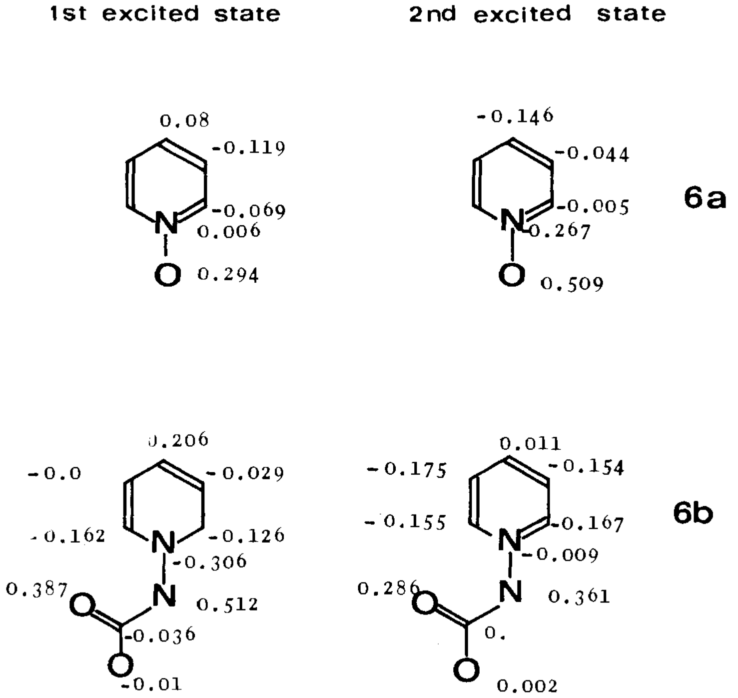
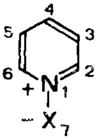


Fig. 6. *Changes in charge distribution between the ground and the first two excited states for pyridine-N-oxide and* **1** *according to a PPP calculation*

In Fig. 6a and 6b are listed the changes in charge distribution $\delta q_\mu = q_\mu^* - q_\mu$ for the first two transitions in pyridine-N-oxide and in **1**. The symbols q_μ and q_μ^* characterize the charge in the ground and first excited states. On excitation negative charge is transferred from the oxygen or ylide-nitrogen to the ring.

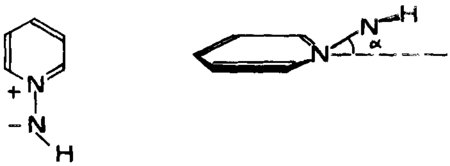
Another interesting result of the PPP calculation is the change in bond orders between position 7 and positions 2 and 6.



X = O, N-CO$_2$C$_2$H$_5$

For pyridine-N-oxide the bond order between oxygen and position 2 increases from –0.26 in the ground state to –0.07 in the first excited state. This is mainly because the highest occupied MO is strongly antibonding between positions 2 and 7 (see Fig. 4). For **1** the bond-orders 2–7 and 6–7 increase from –0.13 in the ground state to –0.02 in the first excited state for the same reason.

For 1-iminopyridinium-ylide **4** (regarded as a simplified model for **1**) we have



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calculated the energy of the ground and first excited states (see Fig. 7) as a function of α (defined as shown above) using an extended *Hückel* model [5]. The increase in bond order between the ylide nitrogen and C(2) or C(6) on excitation to the first excited

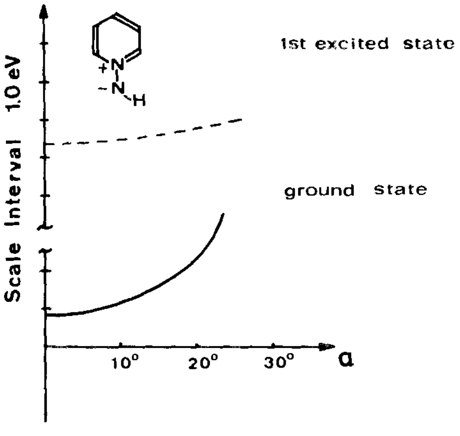

Fig. 7. *Potential energy curve for a displacement of the NH group in* **4** *as a function of* α

state is again in accordance with the idea that ring closure to a diaziridine is favoured in the first excited state as also indicated by the PPP calculation.

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176. Organic Phosphorus Compounds 53
Preparation and Properties of Bis-(chloromethyl)-phosphinic and -thiophosphinic Acid Derivatives as well as Tertiary Phosphine Oxides and Sulfides Containing two $ClCH_2$ Groups [1]

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(27. V. 71)

Summary. Bis-chloromethyl-phosphinates, -thiophosphinates, and -phosphinic amides are formed in fair yield by treating either bis-chloromethyl-phosphinic or -thiophosphinic chloride with alcohols, thiols, or amines in the presence of equivalent amounts of acid binding agents. Unexpectedly, the thiophosphinates show no insecticidal activity and only the β-cumaryl derivative exhibits a low herbicidal activity.

Reduction of bis-chloromethyl-thiophosphinic chloride to bis-chloromethyl-phosphinous chloride is effected with $(PhO)_3P$ at 170°. Interaction of this chloride, $(ClCH_2)_2PCl$, with *Grignard* reagents yields tertiary phosphines, which at slightly above room temperature are unstable, but which may be characterized as oxides or sulfides.

We [2] and others [3] [4] have recently found an easy method for the synthesis of bis-chloromethyl-phosphinic chloride involving reaction of $(HOCH_2)_2P(O)OH$ with excess $SOCl_2$ at 80° [3] [2], or with PCl_5 [4]. This chlorination with $SOCl_2$ effected at room temperature, however, unexpectedly affords bis-chloromethyl-phosphinic anhydride in high yield. Further study of this chlorination shows that the anhydride is also obtained, even at 80°, when only stoichiometric amounts of $SOCl_2$ are used. At room temperature the rate of reaction of the anhydride with $SOCl_2$ is extremely slow,