

MECHANISM OF THE PHOTOCHEMICAL ADDITION-  
SUBSTITUTION REACTIONS OF SIX-MEMBERED  
AZA AROMATIC COMPOUNDS IN HYDROGEN-  
CONTAINING SOLVENTS (REVIEW)\*

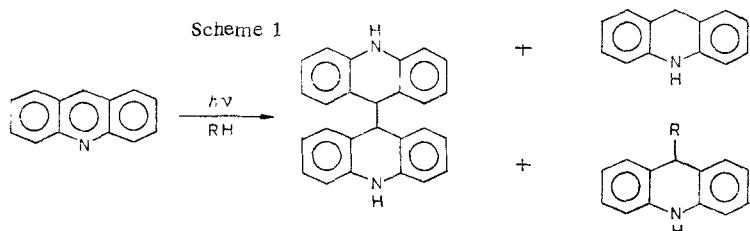
A. Castellano, J. P. Catteau,  
A. Lablache-Combier, B. Planckaert,  
and G. Allan

UDC 541.14:547.821.831.833.  
861.853.852.863.835

The corresponding semiquinone radicals are formed via a one-photon reaction during the irradiation of pyridine, quinoline, isoquinoline, pyrazine, pyrimidine, quinoxaline, and acridine in neutral hydrogen-containing solvents such as ether, methanol, or ethanol. In all cases, the dissolved substance in the  $n\pi^*$ -excited (usually singlet) state splits out a hydrogen atom from the solvent. Six-membered monoaza aromatic compounds on irradiation in methanol acidified with HCl are converted to the same semiquinone radicals as in neutral media, but via a two-photon process consisting of electron transfer from an alcohol molecule to the higher excited triplet state of the protonated monoaza aromatic compound. The corresponding cation radicals are formed by UV irradiation of pyrazine, quinoxaline, and phenazine in methanol acidified with HCl. Six-membered o-diaza compounds of the phthalazine and cinnoline type do not react with ether in the absence of a ketone, which acts as a chemical sensitizer. However, they react with methanol via a two-photon mechanism in which the first step is protonation of the dissolved substance, which is followed by electron transfer.

Many papers devoted to photochemical substitution reactions of aza aromatic compounds with hydrogen-containing solvents have been published in the last decade [1]. Primary reaction products — photoaddition products that are usually unstable under the experimental conditions — were isolated in some cases [1].

The photochemical reaction with acridine has received the most study [1]. Acridan, diacridanyl, and 9-substituted 9, 10-dihydroacridan (scheme 1) are formed in different ratios as a function of the solvent when acridine is irradiated in ether, alcohol, or hydrocarbons.



We have studied photosubstitution in the case of the following reactions. 1) Photosubstitution of pyridine by cyclohexane [2] yielded 2- and 4-cyclohexylpyridines and dicyclohexyl (scheme 2):

\* This paper was presented by A. Lablache-Combier at the Euchem conference on the chemistry of heterocyclic compounds (Grande Motte, France, April 24-27, 1973).

Scientific-Technical University, Lille. Translated from Khimiya Geterotsiklichesikh Soedinenii, No. 7, pp. 867-884, July, 1974.

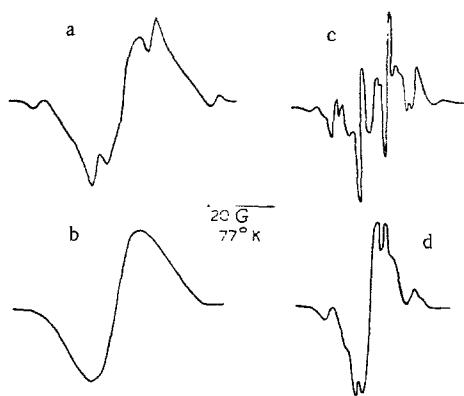


Fig. 1

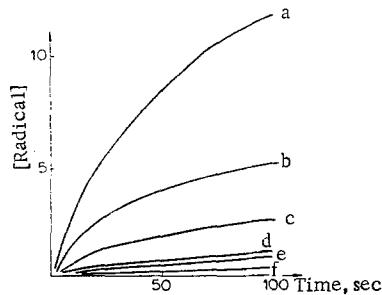


Fig. 2

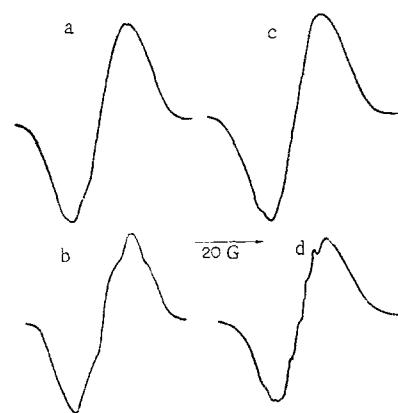


Fig. 3

Fig. 1. ESR spectra: a) 0.1 M solution of quinoline in methanol; b) the same solution 20 min after irradiation; c) 0.1 M solution of quinoline in ether; d) 0.4 M solution of quinoline in ether.

Fig. 2. Kinetics of the formation of radicals from various aza aromatic compounds in 0.5 M methanol solution at 113°K (the concentration units were selected arbitrarily): a) 0.1 M quinoxaline; b) 0.4 M quinoline; c) 0.6 M isoquinoline; d) 1.4 M pyrazine; e) > 1.5 M pyridine; f) > 1.5 M pyrimidine.

Fig. 3. ESR spectra: a) solution of quinoline in CH<sub>3</sub>OH; b) solution of quinoline in CD<sub>3</sub>OD; c) solution of 2-methylquinoline in CH<sub>3</sub>OH; d) solution of 2-methylquinoline in CD<sub>3</sub>OD.

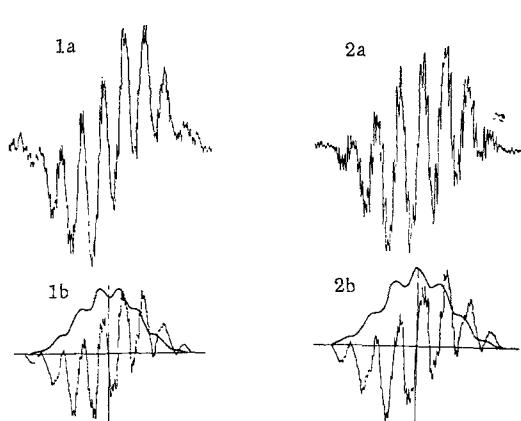


Fig. 4

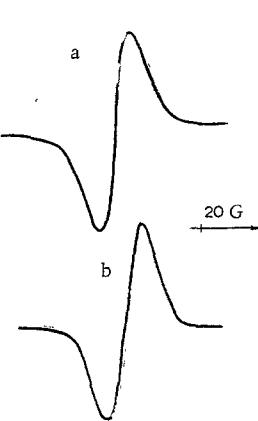


Fig. 5

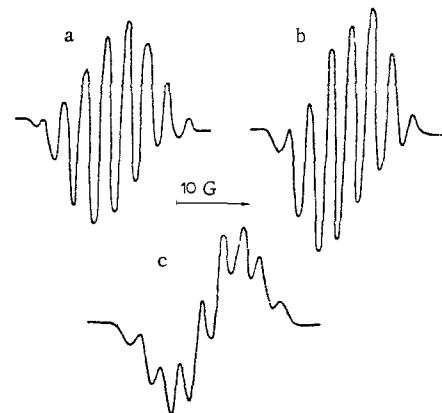
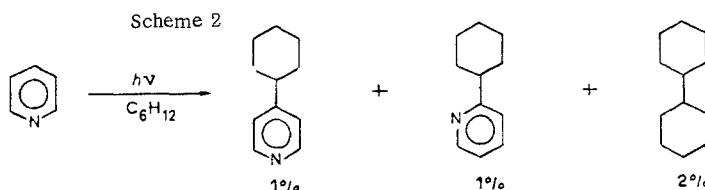


Fig. 6

Fig. 4. ESR spectra: 1) 9-phenylacridine in CH<sub>3</sub>OH; 2) 9-phenylacridine in CD<sub>3</sub>OD; a) experimental spectra; b) theoretical spectra (0.4 M at 193°K).

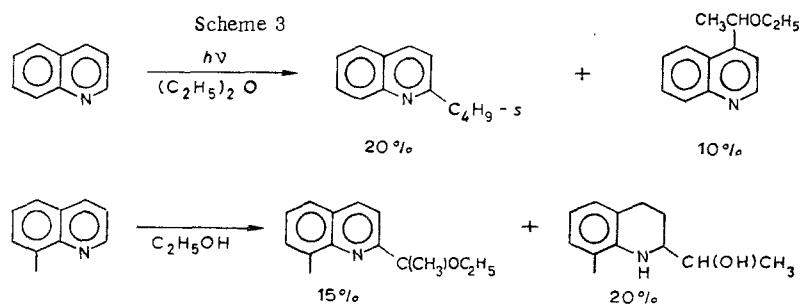
Fig. 5. ESR spectra: 1) 9-phenylacridine in CH<sub>3</sub>OH; b) 9-phenylacridine in CD<sub>3</sub>OD (0.2 M, 113°K).

Fig. 6. ESR spectra of radicals formed during UV irradiation of 0.9 M solutions of 9-phenylacridine: a) radical X-H (CH<sub>3</sub>OH solvent); b) radical X-D (CD<sub>3</sub>OD solvent); c) mixture of radicals X-H and X-D [CH<sub>3</sub>OH + CD<sub>3</sub>OD solvent (1:1)].

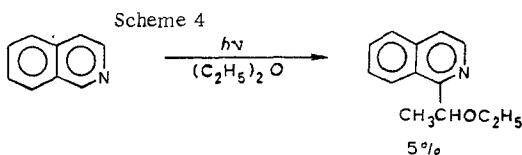


2) The photochemical substitution of quinoline by cyclohexane and of quinoline and some of its methyl-substituted derivatives by ether [3] gave 2- and 4-substituted compounds when methyl groups were absent in these positions. The photochemical reaction of 8-methylquinoline with neutral ethanol gave equal amounts

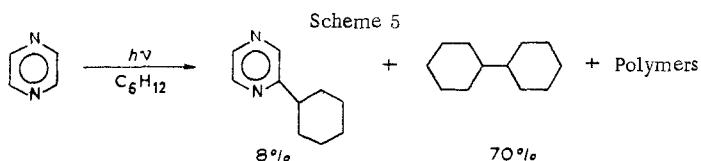
of the 2-( $\alpha$ -hydroxyethyl) derivative and 1,2,3,4-tetrahydroquinoline. Only aromatic compounds are formed in the case of quinoline [4] (scheme 3):



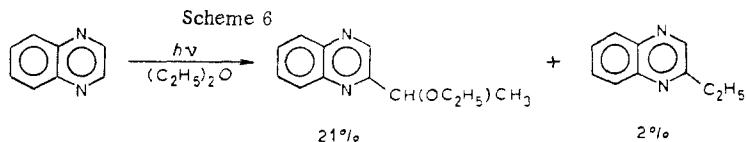
3) In the photochemical substitution of isoquinoline by ether [3], substitution occurs only in the 1 position (scheme 4), and 1-methylisoquinoline does not react:



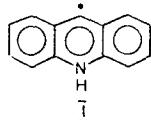
4) In the photochemical substitution of pyrazine by cyclohexane, the products are 1-cyclohexylpyrazine and dicyclohexyl (scheme 5):



5) In the photochemical substitution of quinoxaline by ether, the reaction products [6] are 2-(1-ethoxyethyl)quinoxaline and 2-ethylquinoxaline (scheme 6):



The structures of the compounds obtained suggest a radical mechanism for the occurrence of these photochemical reactions. From the numerous studies devoted to the flash photolysis of acridine, it was concluded that radicals of the I type are intermediates in these reactions [1]. However, 4 years ago, when we began our studies, there had been practically no ESR studies of these photochemical reactions nor spec-



tral studies of the one- and two-ring compounds, and the mechanisms of the photochemical substitution-addition reactions were interpreted in analogy with the photochemical reactions of acridine. Our goal was to confirm that radicals are the intermediate particles in these reactions, to characterize them, and to establish the mechanism of their formation and, consequently, the mechanism of the photochemical substitution-addition reactions.

#### STRUCTURE OF THE RADICALS FORMED IN NEUTRAL MEDIA

Electron-spin-resonance signals are observed when pyridine, quinoline, isoquinoline, acridine, pyrazine, pyrimidine, quinoxaline and some of their methyl-substituted derivatives in ether, methanol, or ethanol are

TABLE 1. Experimental Secondary Moments of Radicals Formed during UV Irradiation of Aza Compounds in  $\text{CH}_3\text{OH}$  and  $\text{CD}_3\text{OD}$  at 113°K

| Compound              | Solvent                | $M_2$ | $\Delta M_2$ |
|-----------------------|------------------------|-------|--------------|
| Quinoline             | $\text{CH}_3\text{OH}$ | 88    |              |
|                       | $\text{CD}_3\text{OD}$ | 76    | 12           |
| 2-Methylquinoline     | $\text{CH}_3\text{OH}$ | 95    |              |
|                       | $\text{CD}_3\text{OD}$ | 82    | 13           |
| 4-Methylquinoline     | $\text{CH}_3\text{OH}$ | 127   |              |
|                       | $\text{CD}_3\text{OD}$ | 114   | 13           |
| 2,4-Dimethylquinoline | $\text{CH}_3\text{OH}$ | 134   |              |
|                       | $\text{CD}_3\text{OD}$ | 121   | 13           |
| Isoquinoline          | $\text{CH}_3\text{OH}$ | 81    |              |
|                       | $\text{CD}_3\text{OD}$ | 73    | 8            |
| 3-Methylisoquinoline  | $\text{CH}_3\text{OH}$ | 82    |              |
|                       | $\text{CD}_3\text{OD}$ | 75    | 7            |

TABLE 2. Experimental Secondary Moments ( $G^2$ ) of Radicals Formed during UV Irradiation of Quinoline and Isoquinoline in Various Solvents at 113°K\*

| Solvent  | Quinoline | Isoquinoline |
|----------|-----------|--------------|
| Methanol | 100       | 92           |
| Ethanol  | 102       | 95           |
| Ether    | 112       | —†           |

\* Calculated with allowance for the fact that  $g = 2.0023$  at 113°K.

† The secondary moment cannot be measured accurately because of the low intensity of the signal.

TABLE 4. Secondary Moments of the Radical Formed during UV Irradiation of 9-Phenylacridine (113°K)

| Solvent         | Secondary moment |             |
|-----------------|------------------|-------------|
|                 | exptl.           | theoretical |
| Methanol        | 42               |             |
| $d_4$ -Methanol | 38               |             |
| Ethanol         | 41               | 31          |
| Ether           | 45               |             |

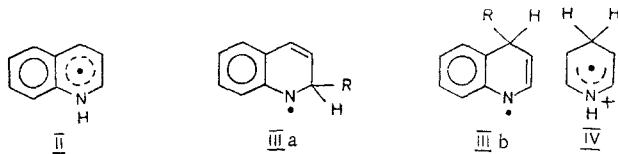
TABLE 3. Theoretical and Experimental Secondary Moments of the Radicals Formed by Irradiation of Some Azo Compounds ( $\text{CD}_3\text{OD}$ , 113°K)

| Compound              | Secondary moment |        |
|-----------------------|------------------|--------|
|                       | theoretical      | exptl. |
| Quinoline             | 72               | 76     |
| 2-Methylquinoline     | 75               | 82     |
| 4-Methylquinoline     | 114              | 114    |
| 2,4-Dimethylquinoline | 116              | 121    |
| Isoquinoline          | 68               | 73     |
| 3-Methylisoquinoline  | 70               | 75     |

irradiated, but only in glass matrices. The ESR signals therefore do not have hyperfine splitting and cannot be analyzed by the usual method. Let us consider the problem of the identification of the structure in the case of quinoline. This method was also used for the rest of the investigated compounds. The broad band of the ESR spectra obtained at 77°K by UV irradiation with a Philips Sp 500 lamp of average pressure of 0.1 M solutions of quinoline in methanol, ethanol, or ether is due to the superimposition of the signals of radicals of the dissolved substance and the solvent [7].

When methanol is used as the solvent, a methyl radical is formed, whereas when ether is used as the solvent, an ethyl radical is formed (Fig. 1, spectra a and c). If the irradiated solution is allowed to stand in the dark, the methyl radicals vanish after 20 min, and only the signal of the radical of the dissolved substance, which does not have hyperfine splitting (Fig. 1b), remains. The concentration of ethyl radicals decreases when a 0.4 M quinoline solution rather than a 0.1 M solution is used. This is a general property. A limiting concentration, above which one cannot detect solvent radicals, exists for each of the investigated compounds. As shown in Fig. 2, one observes a dependence between the kinetics of formation of radicals of the dissolved substance and this limiting concentration. We explain the absence of solvent radicals at high concentrations of the dissolved substance by their rapid recombination. This recombination proceeds more readily when large amounts of radicals are formed (for high concentrations of the dissolved substance) than when small amounts are formed (for low concentrations of the dissolved substance) [6]. (We assume that the solvent radicals are formed as a result of photochemical reaction of the dissolved substance.)

The solvent radicals are not stable enough at 113°K to be detectable by means of ESR spectroscopy, and only the signals of the dissolved substance remain. We carried out all of our subsequent ESR experiments at this temperature. From the structures of the products of the reactions of quinoline with ether [3] and alcohol (scheme 3), two types of radicals — radical II or radicals IIIa, b [7] — can be formed as intermediates in the investigated photosubstitution reactions. The formation of an anion radical is excluded:



As shown in Fig. 3, the ESR signals obtained during UV irradiation of quinoline or 2-methyl quinoline in  $\text{CH}_3\text{OH}$  do not coincide with the signals obtained when  $\text{CD}_3\text{OD}$  is used as the solvent. This is evidence that a portion of the solvent is included in the radical of the dissolved substance.

To confirm the structures of these radicals, we had to use the method of secondary moments. The experimental secondary moment of the ESR signal,  $M_2$ , is

$$M_2 = \int_0^\infty \Delta H^2 G(H) dH,$$

where  $G(H)$  is the absorption curve, and  $H$  is the magnetic field.

It is shown in Table 1 that the difference between the secondary moments in  $\text{CH}_3\text{OH}$  and  $\text{CD}_3\text{OD}$  is almost constant in a single series of quinoline and isoquinoline derivatives. The experimental secondary moments for quinoline and isoquinoline in methanol and ethanol are almost identical (broadening of the spectrum because of the effects of the matrix and saturation of the signal [8] is observed in ether) (Table 2). From the data in these two tables, one can exclude radicals IIIa and IIIb ( $\pi$  or  $\sigma$ ), inasmuch as in radical III ( $\pi$ ), the constant of the interaction of the hydrogen atoms with the  $\text{sp}^3$ -hybridized carbon atom should have a high value. For IV [9] it is 61.6 G and, consequently, the experimental secondary moment should be higher than the observed value. Furthermore, when  $R = \text{CH}_2-\text{OH}$ , the methylene protons are found in the  $\gamma$  position, and their interaction constant is less than 1 G [10]; in this case, the difference between the experimental secondary moments in  $\text{CH}_3\text{OH}$  and  $\text{CD}_3\text{OD}$  should be considerably less than the observed 13 G<sup>2</sup> (Table 1).

In radicals III ( $\sigma$ ), the hyperfine interaction constant of the nitrogen atom should have a value on the order of 50 G — it is 52.5 G [11] for the pyridine cation radical — and the ESR spectrum consequently should be considerably broader than the spectrum observed.

The data in Table 1 and 2 correspond to radical II. To confirm this hypothesis, we calculated the theoretical secondary moment of this radical, in which the nitrogen atom is in the  $\text{sp}^2$ -hybridized state. According to [12], the secondary moment of radicals of the II type is

$$M_2 = M_{2H} + M_{2g} + \frac{\sigma^2}{4} + M_{2N} + M_{2NH},$$

where  $M_{2H}$  and  $M_{2g}$ , respectively, are the contributions of the hyperfine interaction of hydrogen and anisotropy  $g$ ,  $\sigma$  is the width of the band of a single crystal, and  $M_{2N}$  and  $M_{2NH}$  pertain to the hyperfine interaction of the nitrogen atom and the hydrogen atom bonded to it.

In analogy with previous ESR studies, we have assumed that [7]

$$M_{2N-D} \approx 0,$$

$$M_{2H} = \sum_i n_i 174 \rho_i,$$

where  $\rho_i$  is the spin density on the carbon atom bonded to the hydrogen atom,  $n_i$  is the number of hydrogen atoms bonded to carbon atom  $i$ ,  $M_{2N} = 914 \rho^2 N$  ( $\rho_N$  is the spin density on nitrogen),  $\sigma^2/4 = 6 \text{ G}^2$ , and  $M_{2g} = 4 \text{ G}^2$ .

For the methyl derivatives we assumed that  $M_{2\text{CH}_3} = 495 \rho_t^2$ , where  $\rho_t$  is the total spin density associated with the methyl group. The spin densities were calculated by the method in [13], during which we assumed that [7]

TABLE 5. Spin Densities of Semiquinone Radicals Formed from Quinolines and Isoquinolines

| Position | Quinoline | 2-Methyl-quinoline | 4-Methyl-quinoline | 2,4-Dimethyl-quinoline | Isoquinoline | 3-Methyliso-quinoline |
|----------|-----------|--------------------|--------------------|------------------------|--------------|-----------------------|
| 1        | 0,1566    | 0,1320             | 0,1345             | 0,1130                 | 0,4042       | 0,4084                |
| 2        | 0,2109    | 0,1833             | 0,2135             | 0,1825                 | 0,1007       | 0,1095                |
| 3        | -0,0250   | 0,0101             | -0,0443            | -0,0130                | -0,0510      | -0,0495               |
| 4        | 0,3634    | 0,3568             | 0,3726             | 0,3658                 | 0,1507       | 0,1396                |
| 5        | 0,1837    | 0,1966             | 0,1996             | 0,2132                 | 0,1178       | 0,1124                |
| 6        | -0,0065   | -0,0151            | -0,0119            | -0,0209                | 0,1216       | 0,1247                |
| 7        | 0,0791    | 0,0931             | 0,0880             | 0,1036                 | -0,0295      | -0,0334               |
| 8        | 0,1037    | 0,1001             | 0,1115             | 0,1088                 | 0,2476       | 0,2486                |

TABLE 6. Radicals Formed during UV Irradiation of 9-Phenyl-acridine (233°K, liquid phase) and Quinoxaline (113°K, glass)

| Solvent   | 9-Phenylacridine    | Quinoxaline |
|---|---------------------|-------------|
| CH <sub>3</sub> OH                                | X-H                 | VIII-H      |
| CH <sub>3</sub> OD                                | X-D                 | VIII-D      |
| CD <sub>3</sub> OD                                | X-H                 |             |
| CD <sub>3</sub> OD                                | X-D                 |             |
| CH <sub>3</sub> OH (50) - CH <sub>3</sub> OD (50) | X-H (50) - X-D (50) |             |
| CH <sub>3</sub> OH (80) - CH <sub>3</sub> OD (20) | X-H (80) - X-D (20) |             |

$$\alpha_N = \alpha_C + 0.9\beta_{C-C}; \beta_{C-N} = \beta_{C-C}; \lambda = 1.2,$$

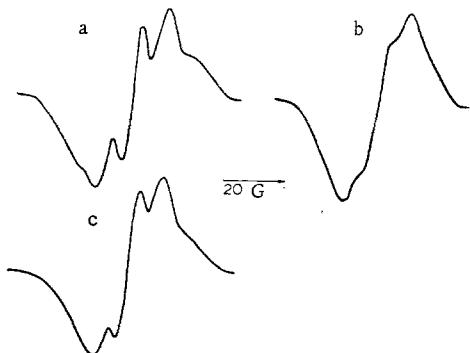


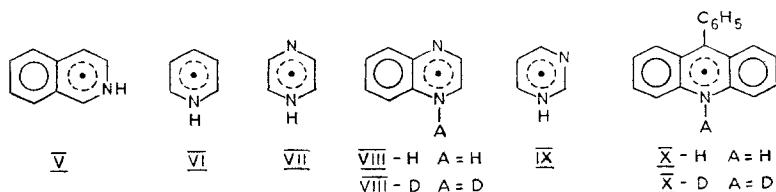
Fig. 7. ESR spectra obtained by irradiation of a 0.4 M solution of 4-methylquinoline: a) in neutral CD<sub>3</sub>OD; b) in a 0.4 M solution of DCl in CD<sub>3</sub>OD; c) in twofold diluted (CD<sub>3</sub>OD) solution b.

where  $\alpha_N$  is the coulombic integral of the nitrogen atom,  $\alpha_C$  is the coulombic integral of the carbon atom,  $\beta_{C-C}$  is the resonance integral of the C-C bond,  $\beta_{C-N}$  is the resonance integral of the C-N bond, and  $\lambda$  is the parameter of the interatomic exchange integral.

To calculate the spin density associated with the methyl group we used a hyperconjugation model with an inductive effect [7].

The experimental and theoretical secondary moments for the II radical or its methyl derivatives coincide satisfactorily in the case of quinolines, and the experimental and theoretical secondary moments for the V radical or its 3-methyl derivative coincide satisfactorily in the case of isoquinolines (Table 3).

On the basis of similar experiments and calculations for other compounds we arrived at the conclusion that on irradiation in ether, neutral methanol, or ethanol, pyridine forms radical VI [2], pyrazine forms radical VII [6], quinoxaline forms radical VIII-H [6], pyrimidine forms radical IX [14], and acridine forms radical I [15], as postulated by flash-photolysis experiments [1]. In all of these radicals the nitrogen atom bonded to the hydrogen atom is  $sp^2$ -hybridized.



In the case of 9-phenylacridine [15], we were able to verify the validity of many of the parameters used in the calculations, inasmuch as this compound forms radicals that are stable in the liquid phase on irradiation in ether, methanol, or ethanol. The experimental spectra of CH<sub>3</sub>OH and CD<sub>3</sub>OD solutions and the calculated spectra coincide (Fig. 4). The radical observed in CH<sub>3</sub>OH is undoubtedly X-H, while that observed in

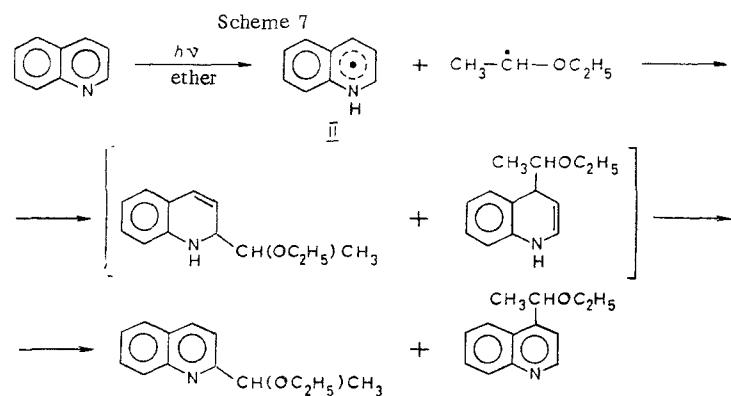
CD<sub>3</sub>OD is undoubtedly X-D. When the experiment is carried out in a glass matrix at 113°K (the conditions under which the spectra of all of the compounds that we studied were recorded), the hyperfine splitting of the signals of the 9-phenylacridinyl radicals X-D and X-H vanishes (Fig. 5), and they take on the form of the signals characteristic for the radicals of other compounds. The experimental secondary moment and the theoretical moment of the X-D radical calculated with the same parameters as those used for quinoline and other investigated compounds are in good agreement [15] (Table 4).

From the results of these experiments we concluded that the parameters used for the calculation of the theoretical secondary moments of the radicals formed from quinoline and other compounds were accurately chosen and, consequently, that the structures postulated by us are correct.

#### MECHANISM OF THE PHOTOCHEMICAL REACTIONS IN NEUTRAL MEDIA

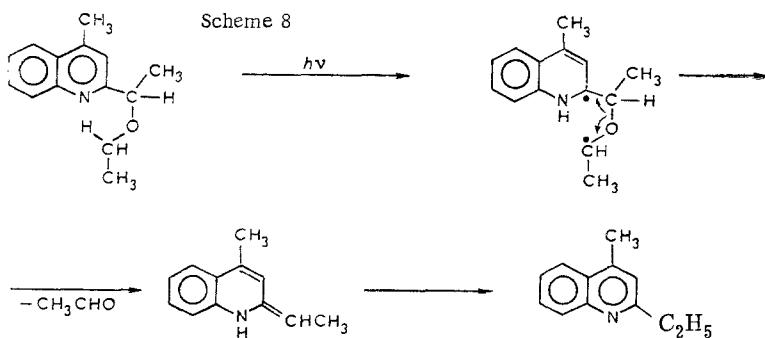
##### Nonpolar Aprotic Hydrogen-Containing Solvents

It is well known that the mechanism of photochemical substitution of six-membered aza aromatic compounds by ether implies splitting out of a hydrogen of the solvent by the nπ\* -excited state of the dissolved substance [1, 16]. All of these reactions are one-photon reactions [8], and their mechanism is similar to the mechanism of the photochemical reaction of quinoline, which is depicted in scheme 7. A dependence exists between the structure of the isolated products



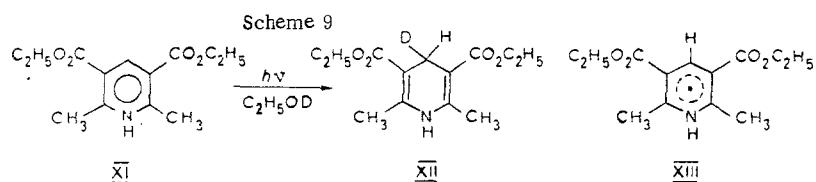
(schemes 1-6) and the spin density calculated for semiquinoline radicals I, II, and IV-X: as shown in Table 5, recombination between the semiquinone radical and the solvent radical for quinoline and isoquinoline occurs at the carbon atoms with the highest spin density (C-2 and C-4 of quinoline, and C-1 of isoquinoline) [7]. Similar dependences were obtained for pyridine [2], pyrazine [5], pyrimidine [14], quinoxaline [6], acridine, and 9-phenylacridine [15].

In the case of 4-methylquinoline [3] and quinoxaline [6], primarily 2-(1-ethoxyethyl) derivatives are obtained in addition to 2-ethyl-substituted compounds (their ratio in the first case is 5 and 40%). It is possible that they are formed not by recombination of the semiquinone and ethyl radicals, which is observed at 77°K by ESR spectroscopy, but rather are the photochemical products of a Norrish reaction of the II type, which takes place with the primary products [3, 4] (scheme 8). If recombination were to occur, ethyl-substituted compounds would be obtained in all cases and one should expect the formation of 4-substituted derivatives.



In polar solvents the  $n\pi^*$  transitions are shifted to lower wavelengths, while the  $\pi\pi^*$  transitions are shifted to higher wavelengths [17], and formation of semiquinone radicals via the same mechanism as in ether or cyclohexane is therefore not apparent. The radicals formed during irradiation of 9-phenylacridine in the liquid phase at 233°K and during irradiation of quinoxaline in a glass matrix at 113°K are shown in Table 6. These compounds were selected because radicals VIII-H and VIII-D, X-H and X-D, or mixtures of them are readily distinguished in them (Fig. 6). In methanol or in deuteromethanol the hydroxyl hydrogen of the alcohol is linked with the nitrogen of the semiquinone radical [18]. Rapid exchange occurs between this hydrogen and the hydroxyl hydrogen of methanol: radical X-D is formed during irradiation of 0.2 M solutions of 9-phenylacridine in a mixture of  $\text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_3$  and  $\text{CH}_3\text{OD}$  even when the methanol concentration is 1%. Similar results were obtained for a 0.4 M solution of quinoxaline at 113°K. When the methanol concentration in ether is 1%, it is absolutely obvious that the first step is photochemical reactions with ether [8].

This sort of rapid exchange, even in a glass matrix at 113°K, seems strange a priori. Kellogg has reported that 1-hydro-4-deutero-3,5-dicarbethoxypyridine is formed in the irradiation of XI in  $\text{CH}_3\text{CH}_2\text{OD}$  (scheme 9). Radical XIII is possibly an intermediate in this reaction and does not exchange the nitrogen-bonded hydrogen for deuterium from the hydroxyl group of the solvent [19, 20].



Because of the rapid exchange, one cannot establish which of the hydrogen atoms of methanol is initially bonded to the nitrogen atom of the semiquinone radical. Consequently, one cannot determine whether the mechanism of the photochemical reactions of six-membered aromatic compounds with methanol is the same as that in the reaction with ether or another solvent. This problem will be solved in the future.

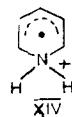
## MECHANISM OF PHOTOCHEMICAL REACTIONS IN HCl-ACIDIFIED ALCOHOL

## Six-Membered Monoaza Aromatic Compounds.

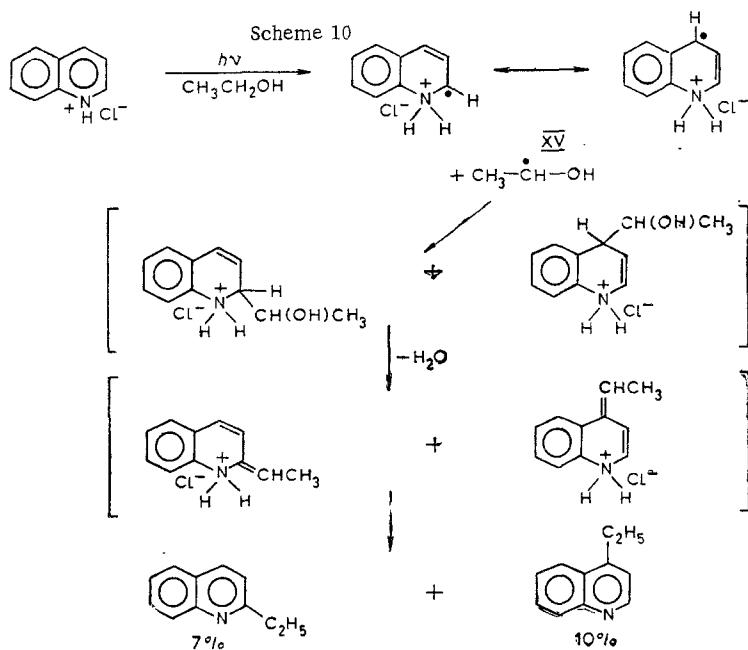
## Structures of the Radicals Formed in

### Acidified Methanol

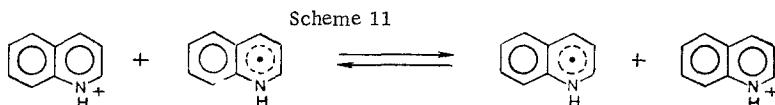
It is considerably more difficult to determine the structures of radicals formed during UV irradiation of six-membered monoaza aromatic compounds in acidified  $\text{CH}_3\text{OH}$  than the structures of radicals formed in neutral solution. The signal for pyridine is small as compared with the noise level. Nevertheless, when the pyridine and HCl concentration is 1.5 M (in  $\text{CH}_3\text{OH}$ ), one can conclude that the ESR spectrum obtained at 113°K does not correspond to radical XIV or to the cyclohexadienyl radical formed by the addition of a hydrogen atom to the ring-carbon atom – in this case the signal would be greater than the observed signal [8, 21]. The spectra obtained in neutral  $\text{CH}_3\text{OH}$  and during irradiation of  $d_5$ -pyridine in  $\text{CD}_3\text{OD}$  and DCl recall the spectra obtained by irradiation of  $d_5$ -pyridine in  $\text{CD}_3\text{OD}$  [2].



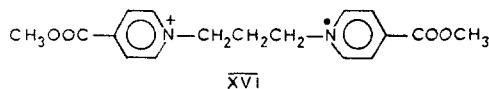
The ESR spectra observed during irradiation of a 0.4 M solution of quinoline in 0.4 M acidified  $\text{CH}_3\text{OH}$  at 113°K are broad bands devoid of hyperfine splitting, but they are narrower than those observed in the spectra of solutions in neutral methanol. This cannot be the signal of a radical of the XV type that was proposed by Stermitz and co-workers to explain the mechanism of the photochemical reaction of quinoline with HCl-acidified ethanol (scheme 10) (other reactions of this type have also been described [1, 4, 8, 21]). The signal of this radical



would be broader than that of radical II and, consequently, that of the observed signal. The ESR spectrum observed during UV irradiation of 0.4 M solutions of 4-methylquinoline in a 0.4 M solution of HCl and CD<sub>3</sub>OD differs from the spectrum of a solution in neutral CD<sub>3</sub>OD, but the recorded spectrum is very close to the spectrum of a solution in neutral CD<sub>3</sub>OD (Fig. 7) upon twofold dilution of the solution with CD<sub>3</sub>OD [8, 21]. Similarly, the spectra of quinoline, isoquinoline, and 9-phenylacridine in HCl-acidified methanol at low acid and solution concentrations coincide with the spectra in neutral methanol. This proves that identical semiquinone radicals are formed during irradiation of six-membered aromatic compounds in neutral and acidified methanol. The narrowing of the signal at high concentrations is associated with electron-exchange processes, as shown in scheme 11 for quinoline, rather than with exchange of the hydrogen atom attached to the nitrogen atom with the solvent. If this sort of exchange occurs sufficiently rapidly, this hydrogen atom will not pair up with the electron. In the case of the deuterium atom, the disappearance of this pairing will have a very slight effect on the form of the spectrum; this does not actually occur (Fig. 7) [8, 21].



We have previously shown that this sort of electron exchange occurs in the case of anion radicals [23] and cation radicals [24], for example, cation radical XVI [25].

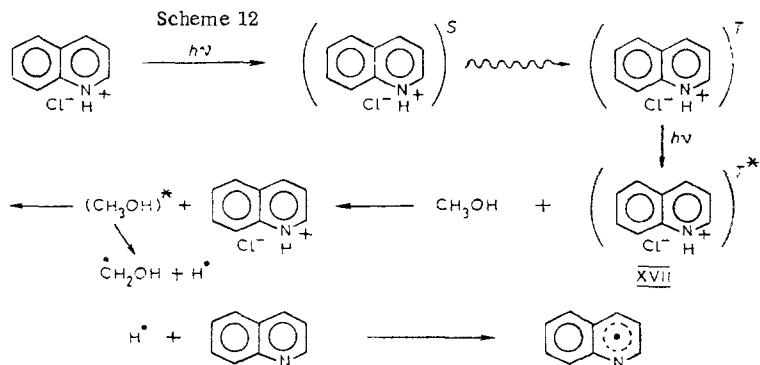


#### Mechanism of Photochemical Reactions

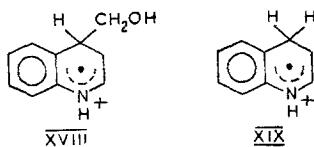
##### in HCl-Acidified Alcohol

The UV irradiation of six-membered monoaza aromatic compounds in neutral and HCl-acidified methanol leads to identical radicals, but their formation in the first case is the result of a one-photon reaction [2, 6-8, 14, 15], whereas in the second case it is the result of a two-photon reaction [8, 21]. Neither semiquinone radicals nor the triplet of the dissolved substances that are observed when HCl is used are observed when hydriodic acid is used. The presence of HI considerably reduces the lifetime of the triplet but has little effect on the quantum yield [26]. This confirms the assumption that in HCl-acidified methanol semiquinone radicals are formed only as a result of two-photon processes and not as a result of simultaneously occurring one- and two-photon processes. Considering the photochemical reactivities of aza compounds — only the  $n\pi^*$  state can readily split out hydrogen [1, 16, 27] — and the fact that semiquinone radicals are

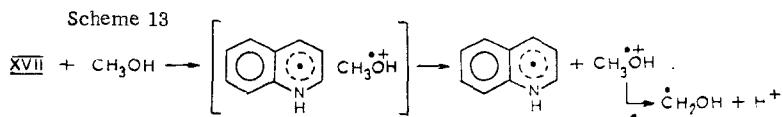
formed in HCl-acidified methanol, it can be concluded that the mechanism of the photochemical reaction of six-membered monoaza aromatic compounds with HCl-acidified ethanol differs from the mechanism proposed by Stermitz in the case of quinoline [22] (scheme 10). The reaction might have occurred through energy transfer from the molecules of the dissolved substance (XVII) to the solvent molecules with subsequent dissociation of the excited state of the solvent molecule and addition of the resulting H<sup>+</sup> radical to the unprotonated molecule, as shown in scheme 12 in the case of the reaction with quinoline. Similar processes involving energy transfer and ethanol dissociation were noted in the irradiation of ethanol solutions of naphthalene [28]. The same mechanism was proposed to explain the photochemical reactions of pyrazolopyrimidines with HCl-acidified methanol [29].



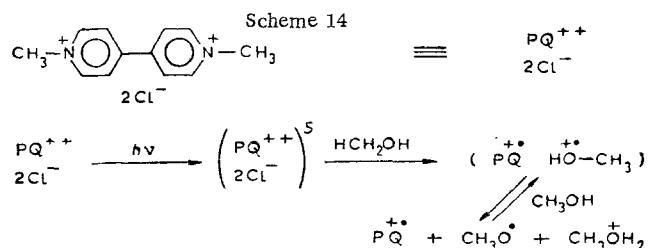
In our case, a mechanism similar to that indicated in scheme 12 is unlikely, inasmuch as very small amounts of the unprotonated aza aromatic compounds remain in the system, and radicals of the XVIII and XIX type were never detected. We will subsequently present a rigorous proof that this sort of energy-transfer process is not realized in the case of phthalazine.



The mechanism presented in scheme 13 for the photochemical reaction of quinoline with HCl-acidified methanol is the most probable mechanism. Electron transfer is realized in this case between methanol and the higher excited triplet state of the protonated form of quinoline. This sort of electron transfer was also previously reported (see review [30]). It takes place, for example, between the singlet excited state of paraquat dichloride and methanol [31] (scheme 14).



Electron transfer does not occur from the chloride ion, inasmuch as chlorine radicals were not detected, and chlorination products were not isolated. This sort of electron-transfer process occurs only from the iodide ion [30, 32].

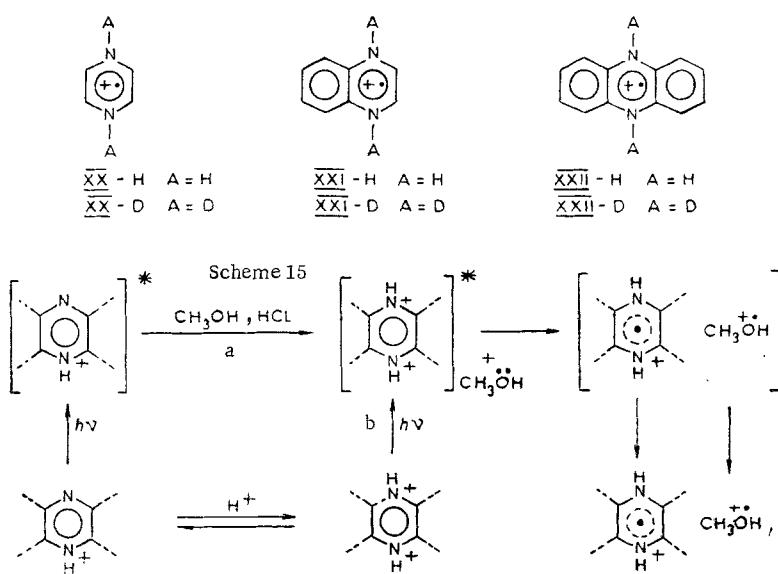


## Mechanism of Photochemical Reactions in Neutral Alcohol

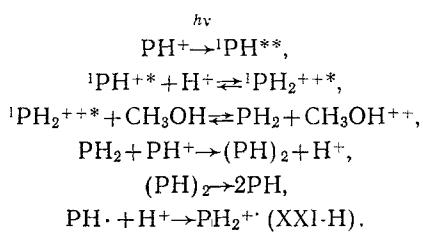
On the basis of the facts that rapid exchange occurs between semiquinone radicals and the hydroxyl hydrogen of alcohol, that the reaction of monoaza aromatic compounds in neutral methanol is a one-photon reaction whereas it is a two-photon reaction in HCl-acidified methanol, and that  $\text{Cl}^-$  does not transfer an electron in HCl media, it can be concluded that the reaction does not occur with electron transfer from  $\text{CH}_3\text{O}^-$  or from  $\text{CH}_3\text{OH}$  to the excited protonated aza aromatic compound. It is more likely that the photochemical reactions in methanol or ethanol proceed in the same way as in ether, i.e., as a result of splitting out of a hydrogen atom of the methyl group by the  $n\pi^*$ -excited state of the dissolved substance in the case of methanol and of a hydrogen atom of the methylene group in the case of ethanol [17]. This sort of equilibrium has already been proven in the case of acridine [1, 16, 33].

### Six-Membered p-Diaza Aromatic Compounds

Pyrazine, quinoxaline, and phenazine are converted to cation radicals XX-H, XXI-H, and XXII-H, respectively, on irradiation in HCl-acidified methanol at 293°K (liquid phase). If the solvent is  $\text{CD}_3\text{OD}$  acidified with DCl, cation radicals XX-D, XXI-D, and XXII-D are formed [18]. The signals of these radicals have good hyperfine splittings, and their ESR spectra have already been studied by Barton and Fraenkel [34].



To explain the formation of these radicals we have proposed a mechanism (scheme 15) that is similar to the mechanism presented in scheme 13. It consists in electron transfer from methanol molecules to photoexcited diprotonated molecules of the diaza aromatic compounds. Inasmuch as this reaction occurs very rapidly, it was not possible to conclude whether it is a one-photon or two-photon reaction. However, it is logical to suppose that electron transfer to diprotonated excited compounds will proceed more readily than to monoprotonated compounds. This mechanism is more likely than the mechanism proposed by Bailey and co-workers for the photochemical reaction of phenazine (P) in strongly acidified methanol [35]:



Transfer of two electrons of the methanol molecule is assumed in the third step of this mechanism, and this is very unlikely. Bailey and co-workers were unable to characterize the  $\text{PH}^{\cdot+}$  radical by either ESR spectroscopy or flash photolysis.

We feel that the photochemical reactions of six-membered diaza aromatic compounds with neutral methanol are one-photon processes [6] that take place due to splitting out of one of the hydrogen atoms of methanol by the  $n\pi^*$ -excited state of the dissolved substance. These reactions proceed in the same way as the reactions of six-membered monoaza aromatic compounds.

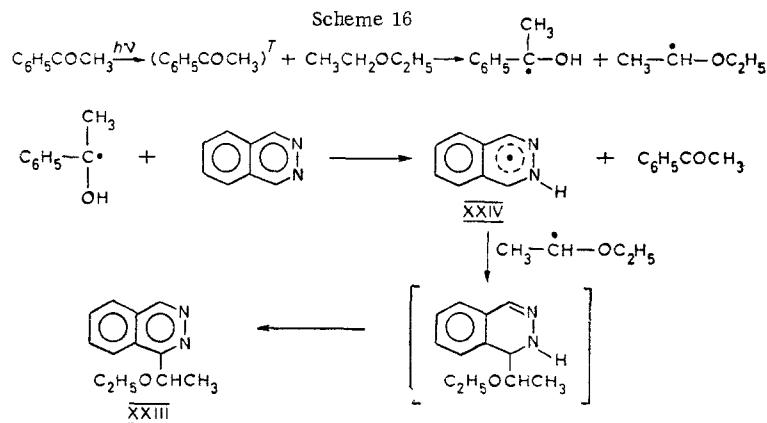
### PHOTOCHEMICAL ACTIVITY OF SIX-MEMBERED *o*-DIAZA AROMATIC COMPOUNDS IN HYDROGEN-CONTAINING SOLVENTS [27]

The behavior of one-ring and two-ring six-membered *o*-diaza aromatic compounds differs from the behavior of other diaza aromatic substances.

Neither pyridazine, phthalazine, cinnoline, nor any of their methyl-, phenyl-, and diphenyl-substituted derivatives react with ether: the formation of products was not observed, and ESR signals were not detected. In the case of phthalazine, XXIII is formed when a ketone is added to a photolyzed solution, and an ESR signal appears. The ketone does not act as a triplet-triplet energy carrier, inasmuch as the quantum yield for phthalazine is one [36], but rather as a "chemical sensitizer" [37]. Precisely this method was used to obtain diadducts of ethers with quinoxaline [6]. The reaction mechanism in the case of phthalazine is depicted in scheme 16. The phthalazinyl radical (XXIV) and its homologs were characterized by means of the method of secondary moments.

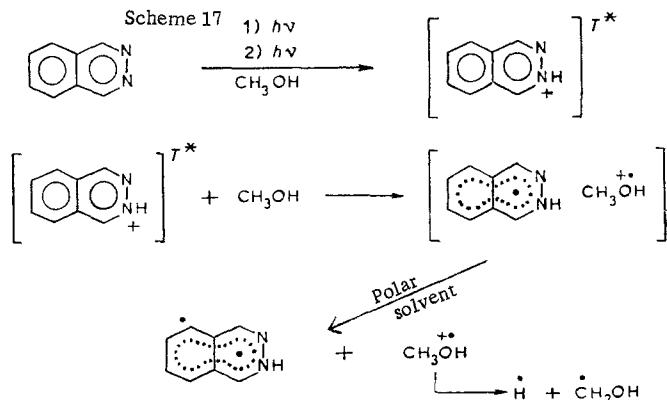
When methanol is used as the solvent, semiquinone radicals are formed as a result of a two-photon process even in the absence of ketone.

The fact that an ESR signal is not detected when ether is used as the solvent proves that the two-photon reaction with methanol is not a charge-transfer reaction with subsequent splitting of methanol into



$\cdot\text{CH}_2\text{OH}$  and  $\cdot\text{H}$  radicals in analogy with scheme 12. Thus, in contrast to naphthalene [28], energy transfer from the excited triplet state to the solvent is impossible for unprotonated *o*-diaza aromatic compounds.

The first step in the photochemical reaction with methanol should be protonation of the *o*-diaza compound with subsequent electron transfer from methanol or from  $\text{CH}_3\text{O}^-$  to the triplet excited state of the monoprotonated aromatic compound. This mechanism in the case of phthalazine is presented



in scheme 17. A triplet state can be detected by ESR spectroscopy only in methanol solution and not in ether solution. This proves that in this case a triplet compound different from phthalazine is observed and is in agreement with the proposed mechanism. The fact that the photochemical reaction is not a one-photon reaction in the presence of  $\text{CH}_3\text{O}^-$  is yet another proof that six-membered monoaza compounds do not react with methanol with electron transfer from the  $\text{CH}_2\text{OH}$  and  $\text{CH}_2\text{O}^-$  molecules to a molecule of the protonated monoaza compound.

## CONCLUSIONS

As a result of this research, it has been established that if the aza aromatic compound has an  $n\pi^*$  state, it is precisely this state that is active, and a one-photon reaction occurs. For quinoline and quinoxaline this is undoubtedly a singlet state, inasmuch as the  $\pi\pi^*$  state is a triplet state [1, 3, 38]. In the case of isoquinoline, this is also possibly a singlet state, inasmuch as the  $S_1$  and  $T_1$  states are  $\pi\pi^*$ -excited states. The difference in energies between the  $S_1(\pi\pi^*)$  and  $S_2(n\pi^*)$  levels is less than between the  $T_2(n\pi^*)$  and  $T_1(\pi\pi^*)$  states [1]. For acridine it has been proven by numerous studies that the photochemical reaction proceeds at least partially with the  $S_1(n\pi^*)$  excited state [1, 16]. Inasmuch as the spectroscopic state of pyridine is unknown, the nature of the  $n\pi^*$  active excited state cannot be proved.

If an  $n\pi^*$  state is not formed during excitation, the photochemical reaction should proceed via a different path. This explains the unusual behavior of phthalazine and other o-diaza aromatic compounds [27], inasmuch as it is known that the singlet states of phthalazine have a very brief lifetime [39] and that a  $\pi\pi^*$  triplet is formed quantitatively during excitation [40]. The reaction proceeds via a two-photon mechanism concluding with protonation, if it is not already realized by an acid of the HCl type, and electron transfer from the oxygen-containing solvent to the higher excited triplet state of the dissolved substance.

This research also opens up the possibility of the use of ESR spectroscopy in the study of several aspects of photochemical reactions in those cases in which flash photolysis and emission spectroscopy do not give information.

The experimental conditions have already been described by us in [2, 3, 5, 8, 15].

## LITERATURE CITED

1. A. Lablache-Combier, in: *Éléments de Photochimie Avancée*, edited by P. Courtot, Hermann, Paris (1972), p. 289.
2. S. Caplain, A. Castellano, J. P. Catteau, and A. Lablache-Combier, *Tetrahedron*, 27, 3541 (1971).
3. A. Castellano and A. Lablache-Combier, *Tetrahedron*, 27, 2303 (1971).
4. F. R. Stermitz, C. C. Wei, and C. M. O'Donnell, *J. Amer. Chem. Soc.*, 92, 2745 (1970).
5. B. Planckaert, *Thèse de 3-eme Cycle*, Lille (1972).
6. A. Castellano, J. P. Catteau, A. Lablache-Combier, B. Planckaert, and G. Allan, *Tetrahedron*, 28, 3511 (1972).
7. G. Allan, A. Castellano, J. P. Catteau, and A. Lablache-Combier, *Tetrahedron*, 27, 4687 (1971).
8. J. P. Catteau, *Thèse de Doctorat des Sciences*, Université des Sciences et Techniques de Lille (1973).
9. H. J. Bower, J. A. MacRae, and M. C. R. Symons, *J. Chem. Soc., A*, 1918 (1968).
10. D. H. Levy and R. J. Myers, *J. Chem. Phys.*, 43, 3063 (1965).
11. R. E. Cramer and R. S. Drago, *J. Amer. Chem. Soc.*, 90, 4790 (1968).
12. G. Vincow and P. M. Johnson, *J. Chem. Phys.*, 39, 1143 (1963).
13. A. D. McLachlan, *Mol. Phys.*, 3, 233 (1960).
14. A. Castellano, J. P. Catteau, A. Lablache-Combier, and G. Allan, *Unpublished Data*.
15. A. Castellano, J. P. Catteau, A. Lablache-Combier, and G. Allan, *Can. J. Chem.* (in press).
16. D. G. Whitten and Y. J. Lee, *J. Amer. Chem. Soc.*, 93, 961 (1971).
17. N. J. Turro, *Molecular Photochemistry*, W. A. Benjamin Inc., New York (1965), p. 59.
18. A. Castellano, J. P. Catteau, and A. Lablache-Combier, *Chem. Commun.*, 1207 (1972).
19. R. M. Kellogg, T. J. Van Bergen, and H. Wynberg, *Tetrahedron Lett.*, 5211 (1969).
20. T. J. Van Bergen and R. M. Kellogg, *J. Amer. Chem. Soc.*, 94, 8451 (1972).
21. A. Castellano, J. P. Catteau, and A. Lablache-Combier (in press).
22. F. R. Stermitz, C. C. Wei, and W. H. Huang, *Chem. Commun.*, 482 (1968).
23. G. L. Malinovski and W. H. Bruning, *J. Amer. Chem. Soc.*, 89, 5063 (1967).
24. S. P. Sorensen and W. H. Bruning, *J. Amer. Chem. Soc.*, 94, 6352 (1972).
25. M. Itoh, *J. Amer. Chem. Soc.*, 93, 4750 (1971).

26. S. Siegel and H. S. Judeikis, *J. Chem. Phys.*, 42, 3060 (1965).
27. A. Castellano, J. P. Catteau, A. Lablache-Combier, and B. Planckaert, *Tetrahedron Lett.* (in press).
28. S. Siegel and K. Eisenthal, *J. Chem. Phys.*, 42, 2494 (1965).
29. M. Ochiai, E. Mizata, Y. Asaki, and K. Morita, *Tetrahedron*, 24, 5861 (1968).
30. A. Lablache-Combier, *Bull. Soc. Chim. France*, 4791 (1972).
31. A. S. Hopkins, A. Ledwith, and M. F. Stam, *Chem. Commun.*, 494 (1970).
32. E. M. Kosower and L. Lindquist, *Tetrahedron Lett.*, 4481 (1965).
33. V. Zanker and G. Prell, *B. Bunsenges. Phys. Chem.*, 73, 791 (1969).
34. B. L. Barton and G. K. Fraenkel, *J. Chem. Phys.*, 41, 1455 (1964).
35. D. N. Bailey, D. K. Roe, and D. M. Hercules, *J. Amer. Chem. Soc.*, 90, 6291 (1968).
36. V. L. Alvarez and S. G. Hadley, *J. Phys. Chem.*, 76, 3937 (1972).
37. P. S. Engel and B. N. Monroe, in: *Advances in Photochemistry*, edited by J. N. Pitts, Jr., G. S. Hammond, and W. A. Noyes, Jr., Vol. 8, Wiley-Interscience (1971), p. 265.
38. J. G. Calvert and J. N. Pitts (editors), *Photochemistry*, Wiley (1966), p. 297.
39. Y. H. Li and E. C. Lim, *J. Chem. Phys.*, 56, 1004 (1972).
40. E. C. Lim and J. Stanislaus, *J. Chem. Phys.*, 53, 2096 (1970).