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PHOTOCHROMISM OF CYCLIC AZIRIDINYLANILS

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Polynuclear heterocyclic systems containing an aziridine ring are effective photochromes; the most important and well studied among them are derivatives of 1,3-diazabicyclo-[3.1.0]hex-3-ene, 1,4-diazabicyclo[4.1.0]hept-4-ene, and 1,1a-dihydroazirino[1,2-a)quinoxaline, all of which we call "cyclic aziridinylanils" (CAA).

The first information on the synthesis of such compounds appeared relatively recently [1, 2]; those reports claimed that photochromism was present in them. Later the photochromic properties were the subject of special investigations [3-8] in solutions, including frozen solutions, in crystals, and in polymeric matrices. In these papers it was shown that under the influence of UV light, the colorless CAA crystals are tinted as a result of opening of the three-membered ring and formation of ylides:



The data from studies on the regioselectivity of 1,3-dipolar addition reactions [9-11] allow us to suggest that the contribution of ylides of type B is small and is additionally lowered with enhancement of the electron-acceptor properties of substituent R. A general disadvantage of the studies performed is the absence of systematized quantitative information on

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the photochromic properties of CAAs; the literature cited above provide values of λ_{max} for absorption of only individual ylides of this class of compounds. This has possibly been the reason that this class of photochromic compounds was not included in the monograph [12], devoted to the topic of photochemistry. Having available a large group of CAAs of diverse structure (I-LXXXV), in this work we set ourselves the goal of studying the photochemistry of these compounds.

For all the CAAs I-LXXXV, on the Specord M-40 spectrophotometer we measured the absorption spectra of their alcohol solutions for concentration of the substances equal to $2-4 \cdot 10^{-5}$ moles·liter⁻¹, and on the Hitachi-330 instrument with integrating sphere of diameter 150 mm we measured the reflectance spectra of powdered samples deposited on an inert white substance which were irradiated beforehand with UV light (and for individual compounds, unirradiated samples) (Table 1). The absorption spectra of the molecular forms (and the corresponding reflectance spectra agree well with them) have been already discussed earlier [11, 13]. The reflectance spectra of the ylides are measured here for the first time. From them it follows that for most CAA ylides, a characteristic feature is the intense asymmetry of the band in the 440-650 nm region with $\Delta v_{1/2}$ 3000-4000 cm⁻¹, in a number of cases having vibrational structure (Δv_{split} ~ 1000 cm⁻¹).

From the data obtained, it especially follows that the overwhelming majority of CAAs have photochromic properties. And even in those cases when this effect is expressed very weakly, such as in compounds IX and XVI, the bathochromic shift of the long-wavelength band is ~200 nm. In the rest of the compounds, this effect is even more significant, and reaches a maximum in derivatives with $R = 4-NO_2$ ($\Delta\lambda \rightarrow 370$ nm). From this it follows that the photochromism of CAA is accompanied by significant redistribution of electron density, possible only for opening of the three-membered ring with formation of ylides. An alternative mechanism involving opening the aziridine ring with formation of radical centers is discarded especially due to the high reactivity of CAA with respect to dipolarophiles. Furthermore, special EPR measurements of irradiated CAA powders* showed the absence of even trace amounts of radical species.

In stabilization of ylides, a determining role is played by the aromatic nucleus for the aziridine ring, which explains the broad range of photochromic effects when the substituent R is varied. Unfortunately, synthesis of dibromides of 4-R-chalcones (synthons of CAA) with electron-donor groups is problematic. Therefore, mainly electron-acceptor R substituents are represented in the CAAs we studied. We may note that introduction of halides (4-C1, 4-Br, 4-F) has virtually no effect on the photochromic properties of the compounds in the entire series. As a rule, ortho R substituents promote the appearance of hypsochromic effects in the spectra of the corresponding ylides, and in the case of $R = 2-NO_2$ (compound XXXV) actually the disappearance of photochromic effects. A special case is the group R = $4-SO_2CF_3$, since its electron-acceptor character is even more pronounced ($\sigma_n = 1.04$ [14] than for the nitro group ($\sigma_n = 0.78$). Introduction of this group induces a regular deepening of the color of the ylide (see compounds XVII, LIV, LXXXI), but this effect is substantially less than in the corresponding nitro derivatives (X, XXXVII, LXV). This should be explained by the fact that different components dominate in the electronic effects of the groups compared: in the SO₂CF₃ group, the induction effect is dominant; in the NO₂ group, the conjugation effect is dominant. This is consistent with the fact that moving the NO2 group to the meta position of the aromatic radical (compound XXXVI), accompanied by its exclusion from the conjugation chain, considerably weakens the photochromic effect. This is such a regular effect that the ylide of the 5-nitro-2-thienyl derivative L has a deeper color than its 5-nitrophenyl analog XXXVII. We know [15] that the thiophene nucleus is characterized by a higher polarizability, and therefore this heterocycle transmits the electron-acceptor effect of the nitro group more effectively than the benzene nucleus.

The role of the substituents R^1 and R^2 in the appearance of photochromism of CAAs is insignificant, even through it cannot be completely eliminated. For example, in the group of derivatives of diazabicycloheptene for a broad set of substituents R^1 (compounds XXXVII-XLV, LV, LVI) it is obvious that introduction of R^1 groups which differ in electronic character causes small changes in the color of the ylides (λ_{max} 592-636 nm). This also occurs in other CAA series (see Table 1). Only introduction of an o-NO₂ group (compounds XXIVa

^{*}The EPR measurements were done by G. D. Movsesyan (Yerevan Physical Institute, Academy of Sciences of the Armenian SSR), to whom we express our thanks.

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| | max | Λ^{2*} | | 243 256 267 | | 258 261 263 263 263 | 245 | 282 284 284 284 284 284 284 287 | 280 280 282 | | 275 241 279 |
| | | R² | | | | | | н 1 ^{2-н} | OCH ₃ | | |
| | lbstituents* | R1 | | H Br Br | | н СЦз г | H HC(CH ₃) (C ₆ H ₆) | | H H OCH _s | | NO ₂ H H |
| M | | R | | Br NO2 | | HONN NNN NNN NNN | ⊖: Diate (Ciano) (Cia | Sol ⁹ =20S | | | Н 2-NO2 NO2 |
| | Compound | | H2 | | CH ₃) ₂ — | | XV/II | XIX b XXb XXba XXVaa* | XXVII.a XXVIII.a XXXa XXXa | | *eIIIVXXX *fVXXXX IIIXXX |
| | ux, nm | 1 |)W | 508 516 623 | M = -C(| 458 474 604 604 604 | 528 I _a R ²) (XX | 520 516 520 | 614 626 588 588 | =CH ₂ | 496 506 508 |
| | λma | A2# | | 245 258 286 | | 246 242 258 275 275 | 280 .CH(C _c I | 285 247 261 258 258 258 | 283 289 286 286 286 | W | 244 245 245 |
| μ, | ubstituents* | R ² | | | | | - = W :(q , | 2-NO, | 2-F CI N(CH ₃) ₂ H | | |
| | | R1 | | Н ^В Н | | н No CCH ₃ | H H CH(CH ₃)—(X1Xa | 포드찌포 | IIII | | III |
| | | R | | H NO ₂ | | Br NNO2 02 20 20 20 | $SO_2 CF_5$ M =(| NO ₂ H Br | DO22 NNNN NNNN | | H Br 3.NO ₂ |
| | Compound | | | | | VII XI XIII XXIII | XVII | XIX a XXa ³ * XXIb XXIb XXIVa | XXVIa XXVIId XXIX/a XXXI | | XXXII ^{3*} |

| Compound | 2 | Substituents | | y mc | tx, nm | Compound | | Substituents* | |) max | wu vy |
|----------------------------------------|--------------------------------------------------------------------------------------------------------------|-------------------------------------------------|------------------------|--------------------------|--------------------------|---------------------------------|----------------------------------------|---------------------------------------------------------------------------|----------------|--------------------------|---------------------------------|
| | R | - K1 | R ² | A2* | В | - | В | R ¹ | R ² | Λ2* | 8 |
| XXXVIII XI.4* | NO22 NO22 | CI 2-NO ₂ | | 285 280 | 909 | XLIXXIX | NO2 NO2 | Br NO2 | | 285 280 | 604 636 |
| XLVIII XLVI XLVI XLVI XLVI | $\begin{array}{c} \mathrm{NO_2}\\\mathrm{NO_2}\\\mathrm{C_6H_5}\\\mathrm{2^2Br}{-4}\mathrm{NO_2}\end{array}$ | 2,4-diOCH ₃ NO ₂ Br | | 285 265 263 263 | 626 634 536 596 | XLIII XLVI XLVII | NO2 NO2 2-Br-4-NO2 2-Br-4-NO2 | OCH ₃ C ₆ H ₅ H NO ₂ | | 277 281 254 278 | 612 606 618 618 618 |
| L. | NO ₂ - S | II | | 336 | 652 | LI4* | 2-F | Н | | 244 | |
| LUI LUI LVI | 2-CF ₃ SO ₂ CF ₃ NO ₂ | $\operatorname{SO}_2 C_3 F_7$ | | 243 250 272 | 480 550 590 | | 2-SCHF ₂ NO ₂ | H SO ₂ CHF ₂ | | 246 280 | 452 610 |
| | | | | | M C ₆ | H ₃ R ² — | | | | | |
| | | II Br | H | 345 | 500 | LVIII | HI | 00 | н п | 350 | 516 |
| LXI LXI LXIII | н Ч | СШ ^в Н | EEE | 348 | 498 525 | | R C F | BC ² | HE | 339 347 | 520 |
| LXV LXVII | NO2 NO2 | NO ₂ | HI | 352 | 632 614 | LXVIII LXVIII | NO2 NO2 | Br CH ₃ | H | | 616 642 |
| LXIX LXXI | NO2 | | 2 P P | 355 362 | 510 616 | LXX | ннй | Br | ad Com | 345 345 | 516 |
| LXXVII | N II 2 | E # 3 | 58 2 | 352 359 359 | 620 540 695 | LXXVII | NO2 NO2 | - Br | | 350 350 350 | 548 548 |
| LXXXI LXXXI | SO ₂ CF ₃ | | NO ² II | 360 360 | 280 580 | LXXXI | $^{2-F}_{NO_2}$ | $SO_{2}CHF_{2}$ | EH2 | 348 338 | 208 208 208 |
| LXXXIII | NO2 | SO2C3F7 | II | 382 | 620 | | | | | | |
| | | | | | M = -C(0) | $CH_{2})_{4}$ | | | | | |
| LXXXIV | NO2 | II I | | 294 | 628 | | | | _ | | _ |
| | | | | | M ==:C(| CH2) 3 | | | | | |
| LXXXV | NO2 | H H | | 298 | 644 | | | | | _ | |
| *The para ² *In the r | substituents eflectance sp | are given ectra of fo | without n rm A, the | umber: band | s. underg | oes a batł | lochromíc shi | [ft by 10-30 | nm compe | tred v | <i>i</i> th |

the absorption spectra. 3*X 605 (MTHF) [4, 8], 580 625 (KBr) [4]; XXa 495 526 (KBr), 485 512 (EtOH) [4]; XXVa 600 645 (KBr), 570 610 (MTHF) [4]; XXXII 545 [8]; XXXVII 605 [8]. **A photochromic effect was not determined.

TABLE 1 (continued)

TABLE 2. Dark Decolorization Time for Crystals of 4,7-Diaryl-1,4-diazabicyclo[4.1.0]hept-4-enes at 20-25°C

| Compound | t, min | Compound | t, min | Compound | t, min |
|----------------------------|--------------------|---------------------|------------------|-----------|------------|
| XXXVII XXXVIII XXXIX | 1550 290 270 | XLI XLII XLIV | 75 240 200 | LV LVI | 200 110 |

and XL) into the aromatic nucleus, independently of their positions in the CAAs, leads to disappearance of the photochromic properties.

The photochromism of CAAs to a certain degree also depends on the structure of the ring annealed with the aziridine (from the bridge groups M). This is clearly apparent when comparing spectra of compounds of different series, containing the $4-SO_2CF_3$ group as the substituent R (compared compounds XVII, LIV, LXXXI). The highest frequency absorption is displayed by ylides of compounds VII-IX with $M = C(CH_3)_2$ and $R \neq NO_2$. With the appearance of $R = NO_2$, the role of the bridge group levels off, probably because the $N_{(1)}$ atom carries an appreciable positive charge and uncouples the bridge group from the basic chromophore system of the ylide.

In the case of diazabicyclohexenes XIX-XXX, we would separate the endo (a) and exo (b) isomers. And even though the difference in the values of λ_{max} for absorption of isomeric pairs of ylides reaches 20 nm, we do not observe a strict correlation with the structure of the bridge group. The lack of unambiguity in the appearance of electronic effects of the R¹, R², and M groups probably is explained by the superposition of steric factors on them, which is reflected in the packing of the molecules in the crystal and consequently in the conformation of the ylides formed and the degree of charge transfer in these ylides. This can explain in particular the fact that for compounds V, XII, LXXXIV, and LXXXV with the appearance of and an increase in the dimensions of the bridging ring, we observe a bathochromic shift for the long-wavelength band of the ylide.

Important photochromic characteristics are the sensitivity of organic molecules to the intensity of the incident light, the dark decolorization time (return of the ylide to the molecular form) and the number of photoconversion cycles. Unfortunately, a study of photochromes in the crystalline state has not made it possible to quantitatively estimate the first characteristic, since it depends substantially on a number of factors, including the degree of grinding, the method of deposition onto the substrate, etc. We can only say that the sensitivity of CAA crystals (especially with $R = NO_2$) to UV light is very high, since their coloration is observed even upon exposure to scattered light; and for maximum illumination of these compounds in the powdered state, 1-2 light pulses from the Luch-M flashlamp are sufficient (light pulse energy 36 J, pulse length 1/2000 sec).

For the same reason, for photochromic crystals a rigorous estimate of the dark decolorization time (return of the ylide to the molecular form) is also difficult. However, since this time is very significant, it can be estimated with low relative error. For the CAA group (Table 2), such an estimate is made as follows. Onto a substrate of diameter 2 cm, we deposited $5 \cdot 10^{-3}$ g of thoroughly pulverized photochromic material. The substrate was placed into a blackened Petri dish. Illumination was done using a Luch-M flashlamp at a distance of 0.5 cm. Disappearance of the color was monitored visually. From Table 2 it follows that the dark decolorization time for compound XXXVII is 26 h. But it sharply drops upon introduction of the substituent \mathbb{R}^1 . In this case, a definite symbatic variation with the electron-acceptor effect of this substituent is observed: The minimum decolorization time of 75 min is characteristic of the dinitro derivative XLI. When $\mathbb{R} \neq 4$ -NO₂ in the CAA, then the sensitivity of the crystals to UV light drops and simultaneously the dark decolorization time increases up to several tens of minutes.

The decolorization rate also depends on the bridge groups: Thus, for 2,2-dimethyl-4phenyl-6-(4-nitrophenyl)-1,3-diazabicyclo[3.1.0]hex-3-ene (X), the time required for return to the molecular form is 12 h [4]. But it reaches several days in derivatives of azirinoquinoxalines. We know [16] that dark decolorization is accelerated with an increase in the sample temperature: In fact, in derivatives of azirinoquinoxalines LXV-LXVII, at 100°C it



Fig. 1. Reflectance spectra of compound X before (1) and after irradiation with UV light for 5 sec (2), 5 min (3), and 30 min (4).

is reduced down to 5-10 min. Experiments were similarly carried out to estimate the number of photocycles. All the samples indicated in Table 2 were held for more than a hundred cycles without visible indications of decomposition, which was confirmed by the TLC method and by the fact that the IR spectra of multiply irradiated and unirradiated samples were identical.

In our previous experiments, CAA crystals were subjected to short (500 µsec) exposure to UV light. Moreover, in a control test on compound X (which was reported earlier [8] as the most light-resistant compound), upon prolonged exposure to UV light (unfiltered light from a PRK-2 mercury lamp), we observe irreversible changes in the spectra (see Fig. 1). It is especially important to note that the ylide band (λ_{max} = 608 nm) appears practically instantaneously. Then a band appears with λ_{max} = 418 nm, whose intensity after 5 min becomes greater than the intensity of the ylide band. For more prolonged illumination, the intensity of both bands drops; and after 0.5 h, only the bands with λ_{max} = 400 nm remain in the spectrum. This is consistent with the results of other investigators [4, 5, 8], according to which the photochromism of CAAs is complicated by secondary processes: isomerization and dimerization.

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