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THE AZO-CHROMOPHOR AS COMPONENT IN PHOTO [2+2]-CYCLOADDITION REACTIONS SYNTHESIS, STRUCTURE AND PE-ANALYSIS OF PLANAR-PARALLEL BISAZO-MOLECULES **

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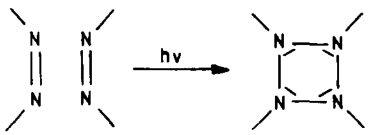
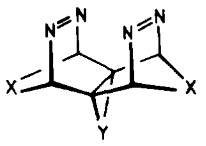
In order to test for a photo [2+2]-cycloaddition between two azo-units a tetracyclic bisazo-compound (7) has been constructed, for which the X-ray analysis confirms a planar-parallel arrangement of the N_2-units and transannular N-N-distances of 2.877 Å and 2.821 Å, resp. In preliminary photoexperiments N_2-elimination predominates in 7; in the N-oxides 10/11 , however, after direct excitation (λ= 254 nm) N_2/N_2O-metathesis (13/14 and 15, resp.) is observed.

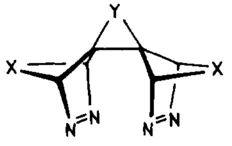
There are good reasons for the N=N-unit not being a common $_{\pi}2$-component in photo [2+2]-cycloaddition reactions 1). In 1977 a first example of an azo/ene-cycloaddition has been reported by Berning and Hünig 2). A photo [2+2]-cycloaddition with two N=N-participants yielding a tetrazetidine-ring (A)-attractive as it would be for preparative as well as theoretical reasons - has not yet been realised. Because of the usually very efficient N_2-elimination 1) such a process has only a chance, if the prerequisites for the cycloaddition are exceptionally favorable. Under these aspects bisazo-molecules with the general structures B and C are being synthesized, in which the stereoelectronic situation (distances, angles) can be influenced systematically by variation of the bridges X,Y 3). In this communication we report results with the bisazo-compound 7 4).



A

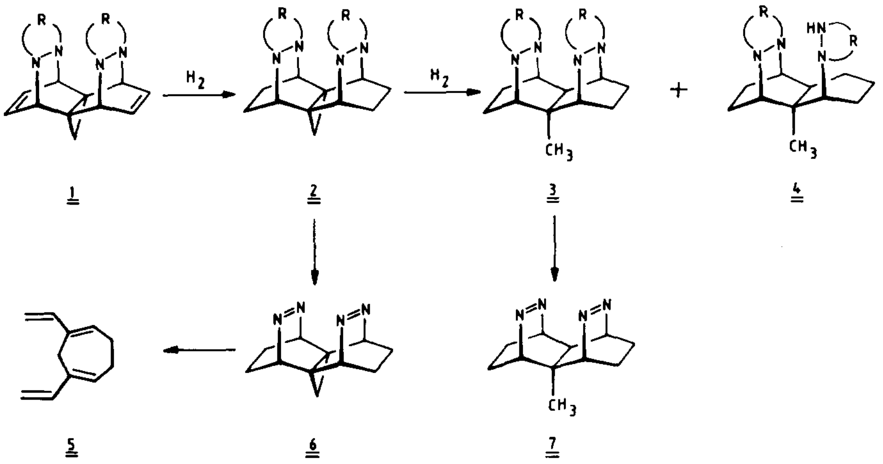


B



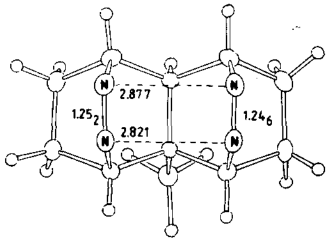
C

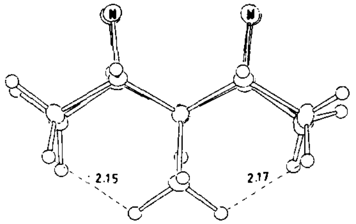
The synthesis of 7 was based on the syn-bisurazole 1 (Ginsburg et al. 5)) and implied as critical step the hydrogenolysis of the sterically well shielded cyclopropane ring in 2. The transformation 2 → 3 is necessary in order to avoid the very facile N_2-elimination expected for the bisazo-compound 6 ($[_{\sigma}2+_{\sigma}2+_{\sigma}2]$)-cycloreversion 6)). Indeed, after hydrolysis of 2 and oxidation the bisvinyl-cycloheptadiene 5 is the exclusive product (85%, colourless, highly reactive liquid). The hydrogenolysis 2 → 3 occurs only under such drastic conditions, that C-N-bond fission (probably 4) is competing. After optimisation (acetic acid, Pd/C (10%), 300 bar H_2, 80°C, 30 h) a 90% yield of a ca. 6:1 mixture of 3 and 4 is achieved, from which 3 (m.p. > 340°C) is separated by crystallisation (methanol). From 3 the yellowish, crystalline and thermally rather



stable (1α,2α,3α,6α,7α,8α)-2-methyl-4,5,9,10-tetraazatetracyclo$[6.2.2.2^{3,6}.0^{2,7}]$tetradeca-4,9-diene (7) is obtained (80%; m.p. 231°C (dec.): $\lambda_{max}(CH_3CN)$= 385 nm (ε= 240) 258 (sh, 260), 239 (610); $J_{6,7}=J_{7,8}=1$ Hz).

According to the X-ray analysis 7) the N=N-units in 7 have a perfect planar-parallel orientation (dev. from the mean plane 0.004 Å) and transannular N-N-distances of 2.877 Å and 2.821 Å, resp. Obviously, the methyl group exerts a noticeable buttressing effect. Under similar conditions effective $[_{\pi}2+_{\pi}2]$- and $[_{\pi}2+_{\sigma}2]$-cycloadditions have been observed 2-4).





In preliminary experiments direct (λ= 254 nm, λ > 280 nm) and sensitised excitation (acetone) of 7 causes N_2-loss (primary products 8/9). However, upon direct excitation of the N-oxides 10/11 (as a ca. 6:4 mixture; λ_{max} (CH_3OH)= 241 nm (ε = 5 000), 388 (125) 8) with monochromatic 254 nm light (CH_3OH, 30°C) the isomers 13/14 (ca. 20%, ca. 7:3) and the symmetrical bispyrazoline 15 (ca. 5%, (1α,4α,7α,10α,13α,14α)-11-methyl-2,3,8,9-tetraazatetracyclo$[8.2.2.0^{4,12}.0^{7,11}]$tetradeca-2,8-dien, m.p. 164°C (dec.), λ_{max} (CH_3OH)= 325 nm (ε= 630); $J_{1,12}=J_{4,12}=10.5$, $J_{1,4} \simeq J_{7,10} \leqslant 1$ Hz) are isolated

(HPLC, silica gel, ethylacetate). An obvious pathway for the N_2/N_2O-metathesis is a

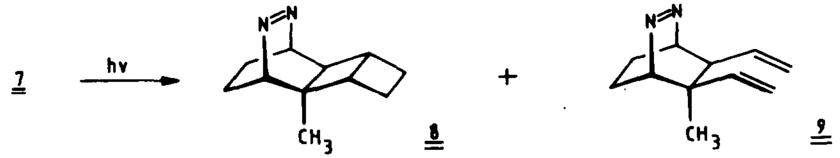
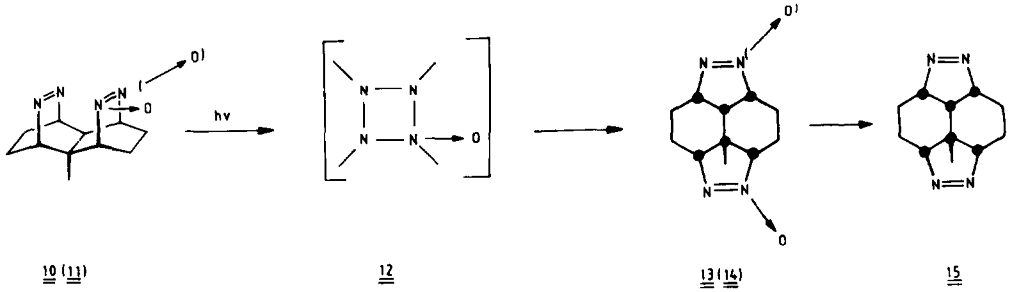
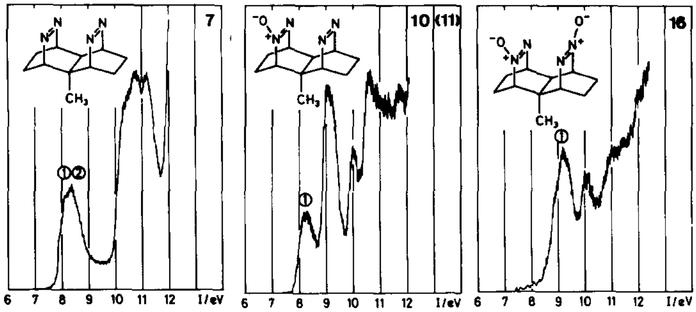
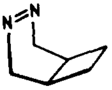


photo [2+2]-cycloaddition and cleavage of the highly strained tetrazetidine-oxides (12) 9). An alternative, though less likely, explanation is that the N_2O-unit participates in this process after its transformation into the oxadiaziridine ring 10) (or its nitrosimine-dipole) or after nitroso/nitren-cleavage.

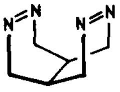


The He(Iα)-PE-spectra of 7, 10/11 and 16 are shown in the Figure. It is an unexpected feature of the PE spectrum of 7 that the interaction of the two n_- lone pair orbital combinations of the two azo groups does not lead to a split of the two bands associated with their in-phase and out-of-phase combinations. The slight broadening of the band① ② ($\overline{I^m_{1,2}}$= 8.3_5 eV) indicates that $I^m_2 - I^m_1 \leq \sim 0.3$ eV. This observation is supported by the PE-spectrum of 10/11 (I^m_1 = 8.3_0 eV), where the band①, due to the n_-^{-1}-ionization process, is again observed at I^m_1= 8.3_0 eV, i.e. at the same place as in the PE spectrum of 8, (I^m_1= 8.2_0 eV) 11,12) within the limits of error. Comparison of the PE-spectra of 10/11 and of 16 (I^m_1= 9.2_0 eV) shows that the second peak in the former is associated with the N_2O group. Finally an STO-3G ab initio calculation for the models D and E, assuming standard geometry, except for the distance between the two N_2 groups in E, which is set equal to the observed one, yields I^m_1= 7.62 eV for D and I^m_1= 7.54 eV, I^m_2= 7.93 eV for E. Note that $\overline{I^m_{1,2}}$= 7.74 eV does not differ significantly from the value obtained for D.





D



E

Experiments are under way, in order to clarify the mechanistic aspects and to check the scope of intra-/intermolecular- N_2-and N_2O-cycloadditions, including systems with mixed homo- and heteronuclear double bonds.

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