Azo-group Stereochemistry and a Correlation with Ultraviolet Absorption Spectra

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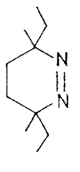
Summary Using M.O. calculations, a correlation is established between the angle subtended by an azo-group and the energy of the $^1(n,\pi^*)$ transition.

Recently the conjugated azo-compound (**4**) was synthesized and found to exhibit its low energy absorption, a presumed $^1(n,\pi^*)$ transition, at an unexpectedly long wavelength.[1] The Frank–Condon maximum of (**4**) occurs at 435 nm, about 100 nm to the red as compared with that found for the five-membered ring analogue (**5**) or that for the unconjugated six-membered ring system (**1**). The only azo-compound with an absorption energy comparable to that for (**4**) is the sterically strained *cis*-azo-2-methyl-2-propane (**8**), which suggested that the variation in transition energy might be steric in origin.



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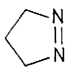

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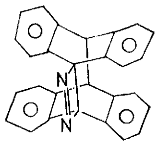

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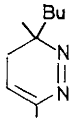

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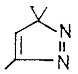

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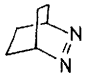

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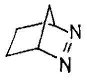

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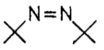

(8)

(**1**) λ_{max} 385 nm (311 kJ mol^{-1}),[8] (**2**) 315 (380),[9] (**3**) <325 (>368),[10] (**4**) 435 (275),[1] (**5**) 350 (342),[11] (**6**) 378 (316),[12] (**7**) 341 (351),[13] (**8**) 447 (268).[14]

To attempt to understand such variations, we have carried out *ab initio* STO-3G M.O. calculations[2] on *cis*-azomethane as a model for the azo chromophore. The calculated energy of the $^1(n,\pi^*)$ transition of *cis*-azomethane was found to be very sensitive to ∠NNC (see dashed line of the Figure). The decrease in excitation energy with increasing angle is due almost entirely to variations in stability of the "*n*" orbital involved in the excitation, rather than the π^*-orbital: increasing ∠NNC forces the two nitrogen lone pairs into closer proximity and thereby increases the lone pair–lone pair interaction.[3] As the interaction increases, the higher or "antibonding" lone pair combination becomes more destabilized in energy, and the energy required to excite (or ionize) an electron from this M.O. decreases.

The calculated $^1(n,\pi^*)$ vertical transition energy for *cis*-azomethane at the calculated optimum NNC angle of 121° is 422 kJ mol^{-1}, compared to the experimental value[4] of 339 kJ mol^{-1}. Since the correlation energy error which gives rise to this discrepancy should remain constant with ∠NNC, the dependence of the *experimental* excitation energy upon angle for unconjugated azo-compounds should be reproduced by a curve parallel to that calculated, but which is lowered by 83 kJ mol^{-1} (see solid line of Figure). Unfortunately, no structural information is known for *cis*-azo-compounds of this type, and thus no *direct* test of the predicted correlation is yet possible.

However, if the decrease in ∠NNC in (**2**) compared to (**1**) is equal to the 12° difference in C=C–C angles between the hydrocarbon analogues cyclohexene[5a] and cyclopentene,[5b] then from the Figure the excitation energy for (**2**) should be *ca.* 68 kJ mol^{-1} greater than in (**1**), in excellent agreement with the observed difference of 69 kJ mol^{-1}. Further, the ∠NNC decrease in the bicyclic compound (**7**) compared to (**6**) should be smaller than the 12° difference for the monocyclic systems, and in agreement the observed increase in transition energy is only 35 kJ mol^{-1} for this pair. One expects that ∠NNC in the sterically strained compound (**8**) should be unusually large and in the range (130—135°) established for *cis*-di-t-butyl ethylenic compounds;[6] in agreement the observed excitation energy for (**8**) fits an NNC angle of 131° on the solid curve of the Figure. Finally, if the decrease in excitation energy due to conjugation is the same in (**4**) and (**5**), and if the decrease in ∠NNC between the pair is equal to the 11° change in C=C–C angle for the analogues cyclohexadiene[7a] and cyclopentadiene,[7b] the transition energy in (**4**) ought to be *ca.* 58 kJ mol^{-1} smaller than in (**5**), again in good agreement with the experimental decrease of 67 kJ mol^{-1}.

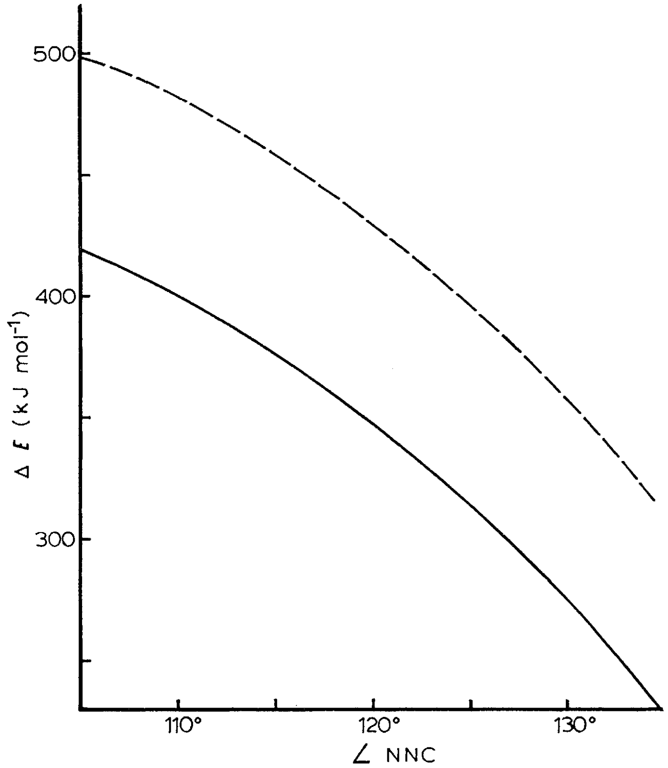

FIGURE. $^1(n,\pi^*)$ *Excitation energy* vs. NNC *angle for* cis *azo-compounds* (*calculated for azomethane* -----; *corrected* ———).

In summary, the predicted dependence of the $^1(n,\pi^*)$ excitation energy upon ∠NNC in azo-compounds seems to be confirmed by the available spectra data. Thus the *cis*-azo-chromophore is unusual in that its low energy absorption varies considerably about the "normal" λ_{max} of *ca.* 360 nm, the extremes probably being (**8**) and (**3**).

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