[5] *R. Hoffmann, E. Heilbronner* & *R. Gleiter*, J. Amer. chem. Soc. *92*, 706 (1970); *P. Bruckman* & *M. Klessinger*, Angew. Chem. *84*, 543 (1972); *R. Gleiter, E. Heilbronner, M. Hekman* & *H. D. Martin*, Chem. Ber. *106*, 28 (1972); *Ch. Batich, P. Bischof* & *E. Heilbronner*, J. Electron Spectrosc. *1*, 333 (1972/73); *R. Gleiter, E. Heilbronner, L. A. Paquette, G. L. Thompson* & *R. E. Wingard, Jr.*, Tetrahedron *29*, 565 (1973); *E. Heilbronner*, Israel J. Chem. *10*, 143 (1972); siehe auch [11].

[6] *P. G. Gassmann, K. T. Mansfield, G. N. Taylor* & *K. B. Wiberg*, Org. Synthesis *49*, 1 (1969); *M. Heyman, V. T. Bandurco* & *J. P. Snyder*, Chem. Commun. *1971*, 297.

[7] *L. Calglioti, E. Foresti* & *L. Riva di Sanseverino*, Tetrahedron Letters *1970*, 1347.

[8] *M. I. Davis* & *T. W. Muecke*, J. phys. Chemistry *74*, 1104 (1970).

[9] *G. Dallinza* & *L. H. Toneman*, Rec. trav. chim. Pays Bas *87*, 805 (1968).

[10] *C. H. Chang, R. F. Porter* & *S. H. Bauer*, J. Amer. chem. Soc. *92*, 5313 (1970).

[11] *P. Bischof, J. A. Hashmall, E. Heilbronner* & *V. Hornung*, Helv. *52*, 1745 (1969).

[12] *L. Pierce* & *Sr. V. Dobyns*, J. Amer. chem. Soc. *84*, 2651 (1962).

[13] *M. J. S. Dewar* & *E. Haselbach*, J. Amer. chem. Soc. *92*, 590 (1970); *N. Bodor, M. J. S. Dewar, A. Harget* & *E. Haselbach*, ibid. *92*, 3854 (1970); *J. N. Murrell* & *A. Harget*, 'Semiempirical SCF-MO Theory of Molecules', Wiley, New York (1972).

[14] *R. Hoffmann*, J. chem. Physics *39*, 1397 (1963).

[15] *B. M. Gimarc*, J. Amer. chem. Soc. *92*, 266 (1969).

[16] *E. Haselbach* & *W. Eberbach*, Helv. *56*, 1944 (1973).

[17] *P. Bischof* & *E. Heilbronner*, Helv. *53*, 1677 (1970).

[18] *D. W. Turner*, Proc. Roy Soc. [London] *A 307*, 15 (1968).

[19] *D. C. Frost* & *J. C. Bünzli*, persönliche Mitteilung.

200. The Photolysis of Tricyclo[4.2.1.0²,⁵]nonadiene: Support of a *Dougherty* 'Type N' Mechanism from Photoelectron Spectroscopical Studies

by **Edwin Haselbach**

Physikalisch-Chemisches Institut, Universität Basel (Switzerland)

and **Wolfgang Eberbach**

Chemisches Laboratorium der Universität Freiburg (Western Germany)

(7. 6. 73)

Summary. In earlier work on the photolysis of derivatives of tricyclo[4.2.1.0²,⁵]nonadiene (I), the intermediacy of a biallyl-like structure has been postulated which is formed by C_1-C_2 bond cleavage of I in its first excited state. This mechanism is now supported by the results of photoelectron spectroscopical studies on I and its two dihydroderivatives. Further support is gained from the theoretically calculated *Ehrenson* C_1-C_2-bond indices for the ground and the first excited state of these molecules. While the results for I in principle can be rationalized on the (one-electron) basis of 'through bond' interaction between the two π-bonds, the absence of C_1-C_2 photocleavage for a substituted tricyclo[4.2.2.0²,⁵]decadiene also requires consideration of an (all-electron) thermochemical driving force.

Derivatives of tricyclo[4.2.1.0²,⁵]nonadiene (I) upon irradiation yield the isomeric tricyclic system II, and in some cases III [1][1].

From the substituent effects on the general course of the photoreaction, as well as from the substitution pattern in the products, it was concluded that the (bisallyl)-radi-

---

[1]   Photochemical studies with the unsubstituted hydrocarbon I are currently under way.

callike intermediate IV is formed in a primary process. Hence, the decisive step in this *Dougherty* 'Type N' reaction [2] is thought to be the cleavage of the C_1-C_2 bond in the first excited state of I, a behaviour rarely encountered in 1,5-dienes.
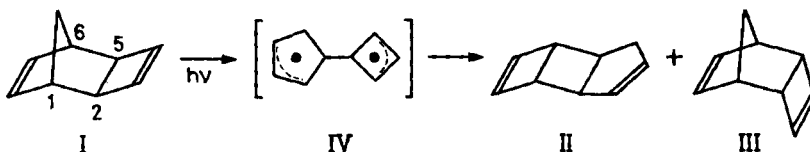
These arguments imply that the C_1-C_2 σ-bond in I which is thermally rather stable, is significantly weakened in the excited state. We wish to point out that such an outcome is indeed expected, in view of the recent photoelectron spectroscopical studies performed by us on I and its dihydro derivatives V and VI [3].
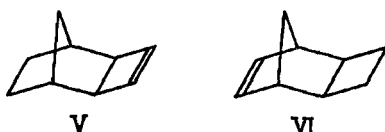
The vertical π-ionisation potentials (IP) were found to be $IP^\pi(V) = 9$ eV and IP^π (VI) $= 8.7$ eV, the difference in π-basis orbital energies (assuming *Koopmans'* theorem [4] to hold) thus amounting to $\Delta A^\pi = 0.3$ eV. For I the first two IP's are IP_1^π (I) $=$ 8.7 eV and IP_2^π (I) $= 9.8$ eV, with $\Delta IP^\pi(I) = 1.1$ eV. Since $\Delta IP^\pi(I) \gg \Delta A^\pi$, a considerable interaction between the π-orbitals of I must take place. In view of the large distance separating them (3.5 – 4 Å), this result provides a further striking example for the now well documented 'through bond' interaction concept, introduced originally by *Hoffmann* [5]. Specifically, in I the bond orbitals of the C_1–C_2 and the C_5–C_6 σ-bonds will serve as 'relay stations' in close analogy to the case of *trans*-tricyclo-[4.2.0.0^{2,5}]octadiene discussed previously [6].
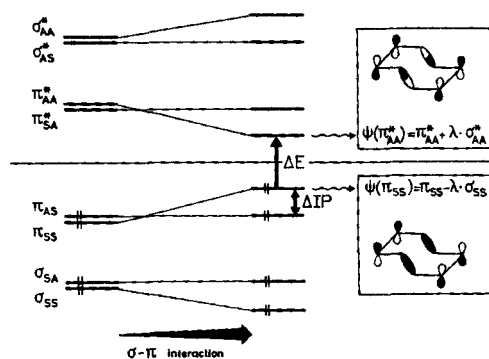

Fig. *Orbital pattern of I, using 1,4-cyclooctadiene* (hypothetical chair conformation; C_{2h}-symmetry) *as a model system*

The Fig. sketches the orbital pattern of I, using for convenience the relevant σ/σ^*- and π/π^*-bond-orbitals of the model system 1,4-cyclooctadiene (hypothetical chair

conformation, C_{2h}-symmetry) as a basis set. (The symmetry labels of the symmetry-adapted semilocalized orbitals refer to the two-fold axes and the mirror plane in that order).

Evidently, after 'turning on' σ-π-interaction, π_{SS} mixes with σ_{SS}, the former being pushed up in energy. As a result, the (observed) gap ΔIP is formed. Furthermore, this interaction yields the final delocalized MO $\psi(\pi_{SS})$ with *bonding character* for the C_1–C_2 and C_5–C_6 π-bonds. It is reasonable to assume that similar interactions occur in the unoccupied manifold. Here, $\psi(\pi^*_{AA})$ results from the in-phase admixture of a fraction λ of σ^*_{AA} to π^*_{AA}. The low lying orbital $\psi(\pi^*_{AA})$, together with the high lying counterpart $\psi(\pi_{SS})$, suggests a significant decrease in excitation energy ΔE (Fig.) with respect to V or VI. Indeed, the 3,4-dicarbomethoxy derivative of I absorbs at $\lambda = 267$ nm ($\varepsilon = 1970$) while the corresponding diester of V has $\lambda = 239$ nm ($\varepsilon = 6400$) [7]. Most relevant for our discussion is that $\psi(\pi^*_{AA})$ of I now has *antibonding* character in the region of the C_1–C_2, C_5–C_6 σ-bonds. We therefore can draw the qualitative conclusion that (*i*) ionization of an electron from $\psi(\pi_{SS})$ weakens these latter bonds, and (*ii*) this weakening is even more pronounced after promotion of I to its first excited state (I*) to which the configuration $[\ ]^2\ [\ ]^2 \ldots [\psi(\pi_{SS})]^1\ [\psi(\pi^*_{AA})]^1$ is presumably the dominant contribution. These conclusions support the postulated photolysis mechanism discussed in the introductionary section.

In order to strengthen these qualitative arguments we have embarked on a calculation of the *Ehrenson* bond index b_{12} [8] of the C_1–C_2 σ-bond in I, V and VI for the ground and the lowest excited state, using MINDO/2- [9] wave functions.

The bond index b_{AB} between two atoms A and B is defined [8] as:

$$b_{AB} = \sum_i^{\substack{\text{occ. MO's}}} \sum_\mu^{\substack{\text{at A}}} \sum_\nu^{\substack{\text{Basisfct.}\\\text{at B}}} n_i\, c_{\mu i}\, c_{\nu i}\, S_{\mu\nu},$$

n_i = occupation number of i-th MO.

$S_{\mu\nu}$ = overlap integral between basis functions φ_μ at A, φ_ν at B.

$c_{\mu i}$, $c_{\nu i}$ = LCAO-coefficients of φ_μ and φ_ν in i-th MO.

The index b_{AB} is rotationally invariant and was designed for theoretical procedures which neglect integral overlap and therefore are not suited for a *Mulliken* population analysis. It has proven most valuable in correlations between bond lengths and bond strength of hydrocarbons, being only slightly inferior to 'ab-initio' bond populations [8] [10].

The following results were obtained:

$b_{C_1-C_2}$	I	V	VI
ground state	0.66	0.66	0.66
excited state	0.60	0.64	0.64

It follows that the decrease in C_1–C_2 bond strength upon I → I* excitation is quite significant when compared with the values for V and VI. Note, however, that these latter systems also show a slight decrease of $b_{C_1-C_2}$ upon excitation, signifying σ-π mixing of the same type as that discussed for I (Fig.). Using second order perturbation

theory it can be shown that such an interaction takes place, albeit to a smaller extent than in I. In agreement with this, the C_1–C_2 bond in V and VI does not exhibit photolytical activity[2]). Nevertheless, it should be kept in mind, that the thermochemical driving force for these reactions is less pronounced than that for I, the corresponding intermediate biradicals being less stabilized than IV by the amount of one allylic resonance energy of $\sim$ 12 kcal/mol [11]. Preliminary studies with a derivative of tricyclo[4.2.2.0^{2,5}]decadiene (VII) also showed no evidence for photochemical C_1–C_2

VII   VIII
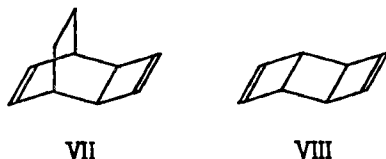
bond cleavage [7]. This suggests that in discussing the elusive I* → IV reaction, one has also to consider a thermochemical driving force due to reduction of strain in the norbornene skeleton of I. Indeed, the difference in strain energies between norbornene and bicyclo[2.2.2]octene amounts to $\sim$ 8 kcal/mol [12]. Conversively, for VIII* one might predict cleavage of C_1–C_2 to be a favorable reaction path. Here, however, the allowed disrotatory ring opening to ground state bicyclo[4.2.0]octatriene will provide a strong alternative, being accompanied by effective removal of two 4-membered rings.

REFERENCES

[1] *W. Eberbach & H. Prinzbach*, Helv. *50*, 2490 (1967); *W. Eberbach*, Chimia *25*, 248 (1971); *W. Eberbach & M. Perroud-Argueilles*, Chem. Ber. *105*, 3078 (1972); *W. Eberbach*, in preparation.
[2] *R. C. Dougherty*, J. Amer. chem. Soc. *93*, 7187 (1971).
[3] *F. Brogli, W. Eberbach, E. Haselbach, E. Heilbronner, V. Hornung & D. M. Lemal*, submitted for publication in Helv.
[4] *T. Koopmans*, Physica *1*, 104 (1934); *W. G. Richards*, Int. J. Mass Spectr. *2*, 419 (1969).
[5] *R. Hoffmann*, Acc. chem. Res. *4*, 1 (1971); *E. Haselbach & A. Schmelzer*, Helv. *55*, 1745 (1972).
[6] *R. Gleiter, E. Heilbronner, M. Hekman & H.-D. Martin*, Chem. Ber. *106*, 28 (1973).
[7] *W. Eberbach*, unpublished results.
[8] *S. Ehrenson & S. Seltzer*, Theor. chim. Acta *20*, 17 (1971).
[9] *M. J. S. Dewar & E. Haselbach*, J. Amer. chem. Soc. *92*, 590 (1970); *N. Bodor, M. J. S. Dewar, A. Harget & E. Haselbach*, ibid. *92*, 3854 (1970); *J. N. Murrell & A. Harget*, 'Semiempirical SCF-MO Theory of Molecules', *Wiley*, New York (1972).
[10] *J. W. McIver, P. Coppens & D. Nowak*, Chem. Phys. Letters *11*, 82 (1971).
[11] *A. B. Trenwith*, Trans. Farad. Soc. *66*, 2805 (1970).
[12] *N. L. Allinger & J. T. Sprague*, J. Amer. chem. Soc. *94*, 5734 (1972).

[2]) For 3,4-dicarbomethoxy substituted V, efficient dimerization is the only observed process [7].