Tetrahedron Letters No. 23, pp 1953 - 1956, 1974. Pergamon Press. Printed in Great Britain.

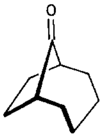
EVIDENCE FOR STRONG NONBONDED n/π INTERACTION IN BICYCLO [4.2.1] NONA-2,4,7-TRIEN-9-ONE [1]

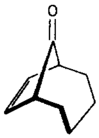
Werner Schäfer, Hartmut Schmidt, and Armin Schweig [+]
Fachbereich Physikalische Chemie der Universität
D-3550 Marburg/Lahn, Biegenstrasse 12, Germany

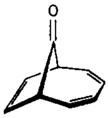
Reinhard W. Hoffmann and Hans Kurz
Fachbereich Chemie der Universität
D-3550 Marburg/Lahn, Lahnberge, Germany

(Received in UK 18 April 1974; accepted for publication 24 April 1974)

Below we offer evidence based on photoelectron(pe)spectroscopy that bicyclo [4.2.1] nona-2,4,7-trien-9-one [2,3] (3) is not a bicycloconjugated (bicycloconjugation [4] = interaction between all formally isolated π segments) molecule. Instead of bicycloconjugation, however, we have been able to detect a novel type of strong nonbonded interaction between the oxygen lone pair MO and the highest occupied MO of the butadiene moiety, in this system.

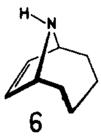

1

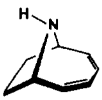

2


3


4


5


6


7

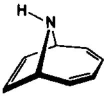

8

Figure 1 shows the pe spectra of 1, 2, and 3 with interpretation. The bands in the spectra of 2 and 3 were assigned by direct comparison with the spectra of 1, 4 [5] and 5 [6] in conjunction with quantum chemical calculations [7-1o]. The details are given in ref. 1o.

Three sorts of interaction between the formally isolated ethylene, butadiene, and carbonyl segments in 3 may be considered: (1) the mutual inductive interaction, (2) the conjugative interaction between the symmetric π MOs, $\pi_{2,s}$ [11], $\pi_{4,s}$ [11], and the carbonyl π MO (i.e. bicycloconjugation), and (3) between the antisymmetric n_a [11] and $\pi_{4,a}$ [11] MOs (i.e. nonbonded n/π interaction). We now discuss these possible interactions by means of the correlation diagram [12] of Figure 2.

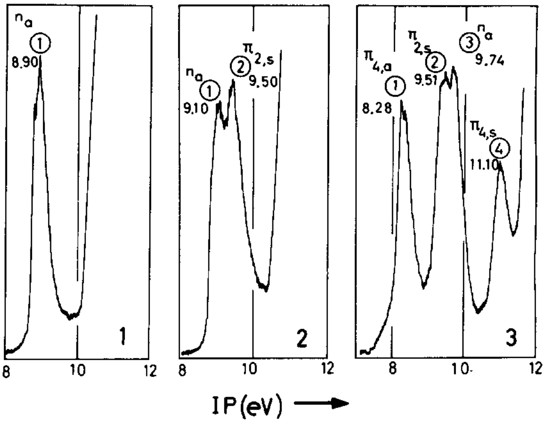
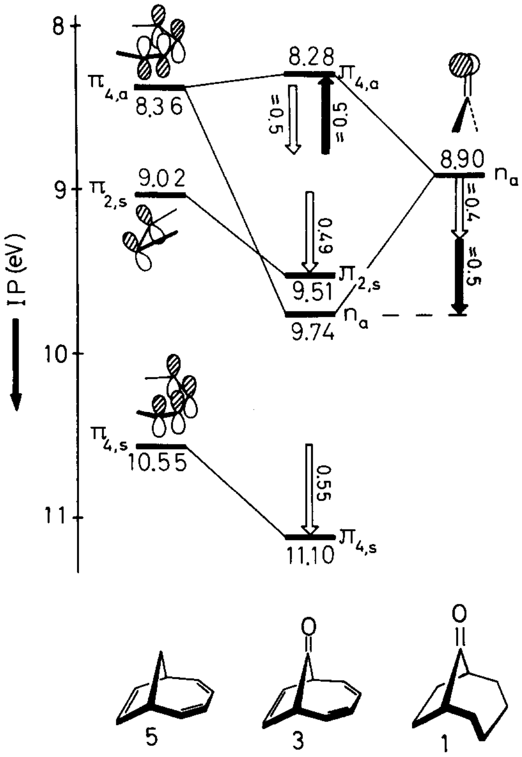


Figure 1

Photoelectron spectra [14] of molecules 1 to 3 with interpretation.[10] The numbers associated with each band are vertical ionization potentials(eV).

Since $\pi_{2,s}$ in 2 and in 3 lie at the same energy it must be concluded that in 3, there is neither homoconjugative interaction between $\pi_{2,s}$ and $\pi_{4,s}$ nor bicycloconjugation. From previous experience with 6, 7, and 8 we know that the inductive influence of the nitrogen bridge on $\pi_{2,s}$, $\pi_{4,a}$ and $\pi_{4,s}$ is nearly the same [4]. As seen from Figure 2, the same appears to be true in 3 since the inductive stabilizations of $\pi_{2,s}$ and $\pi_{4,s}$ due to the carbonyl group have nearly identical values (white arrows). Therefore, if the well-founded assumption is made that the inductive stabilization of $\pi_{4,a}$ in 3 is again $\approx$0.5 eV (white arrow) then $\pi_{4,a}$ must have been simultaneously destabilized by $\approx$0.5 eV (black arrow), through nonbonded interaction with n_a. In full accord with this result is the low energy of n_a in 3, which is partly due to inductive lowering ($\approx$0.40 eV, white arrow) caused by the ethylene and butadiene units [4] and partly to nonbonded conjugative lowering ($\approx$0.5 eV, black arrow).

In order to support the novel type of interaction in 3 theoretically we used a method [13] which permits one to interrupt the conjugation of a selected portion of molecule with the rest of the system in conjunction with the MINDO/2 method. The results are shown in Figure 3. Obviously, there is no trace of bicycloconjugation in 3, but instead nonbonded $n_a/\pi_{4,a}$ conjugative interaction (calcu-



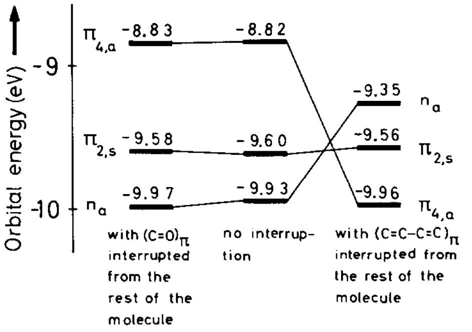


Figure 3
MINDO/2 [9] calculations on 3 at three stages of conjugative interruption.

Figure 2
Correlation diagram for key occupied MOs of 1, 3, and 5. The white and black arrows represent the inductive and conjugative effects (eV), respectively. The numbers shown at the levels are vertical ionization potentials (eV).

lated energy lowering of n_a = 0.58 eV in excellent agreement with the pe value ≈ 0.5 eV). The greater calculated rise in the $\pi_{4,a}$ energy reminds us of the presence of simultaneous hyperconjugative interaction.

References

1 Part 49 of "Theory and Application of Photoelectron Spectroscopy". This work was supported by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie.-Part 48: A.Schweig, H.Vermeer, and U.Weidner, submitted for publication.

2 T.A.Antkowiak, D.C.Sanders, G.B.Trimitsis, J.B.Press, and H.Shechter, J.Amer. Chem.Soc. 94, 5366 (1972).

3 The pe spectrum of 3 has also been studied by J.C.Bünzli, D.C.Frost, and L. Weiler, submitted for publication. We wish to thank Professor Weiler for sending a preprint of this paper.

4 H.Schmidt, A.Schweig, A.G.Anastassiou, and H.Yamamoto, Chem.Commun., in press.

5 P.Bischof, J.A.Hashmall, E.Heilbronner, and V.Hornung. Helv.Chim.Acta, 52, 1745 (1969).

6 P.Bischof, R.Gleiter, and E.Heilbronner, Helv.Chim.Acta, 53, 1425 (1970).

7 J.A.Pople and D.L.Beveridge, "Approximate Molecular Orbital Theory", McGraw-Hill, New York, 1970.

8 Version = PSS1, K.W.Schulte and A.Schweig, Theoret.chim.Acta, in press.

9 M.J.S.Dewar, "The Molecular Orbital Theory of Organic Chemistry", McGraw-Hill, New York, 1969.

10 Band ① in the spectrum of 1 is necessarily due to ionization from the orbital containing the oxygen lone pair (n_a [11]). Bands ① and ② in the spectrum of 2 must then be ascribed to ionization from n_a and the ethylenic π MO ($\pi_{2,s}$ [11]), respectively. This interpretation means that the π level is stabilized by 0.53 eV relative to the π level in 4 (8.97 eV [5]) and the n_a level by 0.20 eV relative to its counterpart in 1, through mutual inductive interaction between the ethylenic and carbonyl double bonds. Assignment of bands ① and ④ in the spectrum of 3 is made by comparison with the spectrum of 5 [6]. Accordingly, band ① is due to ionization from the highest occupied butadiene π MO, $\pi_{4,a}$ [11] (in 5, $\pi_{4,a}$ is located at 8.36 eV) and band ④ to the lowest occupied butadiene π MO, $\pi_{4,s}$ (in 5, $\pi_{4,s}$ is located at 10.55 eV). Finally, bands ② and ③ are ascribed to ionization from the $\pi_{2,s}$ and n_a MOs respectively, on two arguments: (1) all all-valence electron calculations performed place $\pi_{2,s}$ above n_a [predicted respective energies (in eV): CNDO/2 [7] = -12.08, -13.31; INDO [7] = -11.73, -12.81; CNDO/S [8] = -9.69, -10.50; and MINDO/2 [9] = - 9.60, -9.93; measured [12] = -9.51, -9.74] and (2) from the measured inductive stabilization of $\pi_{2,s}$ in 2, $\pi_{2,s}$ in 3 is expected to be located at 9.55 eV, in good agreement with the found value of 9.51 eV.

11 The MOs are classified in terms of the segment (2=ethylene, 4=butadiene) on which they are mainly localized and in terms of the molecular plane of symmetry (s = symmetric, a = antisymmetric).

12 Based on the validity of Koopmans' theorem: T.Koopmans, Physica 1, 104 (1934).

13 C.Müller, A.Schweig, and H.Vermeer, Angew.Chem., in press. For further recent applications of the method, see: H.Schmidt, A.Schweig, and A.Krebs, Tetrahedron Lett., in press and W.Schäfer, A.Schweig, G.Maier, T.Sayrac, and J.K. Crandall, ibid, in press.

14 The HeI (584 Å) photoelectron spectra were recorded on a PS-18 spectrometer from Perkin-Elmer, Beaconsfield (England).