4692 J. Org. Chem. 1995, 60, 4692−4696

Articles

Electronic and Geometrical Structure of Bicyclo[8.1.0]undec-1(10)-en-5-yn-11-one and Related Compounds

R. Gleiter,* M. Merger, A. Altreuther, and H. Irngartinger

Organisch-Chemisches Institut der Universität Heidelberg, Im Neuenheimer Feld 270,
D-69120 Heidelberg, Germany

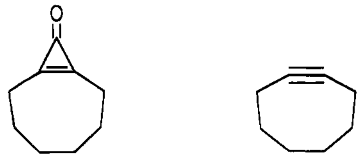
Received January 26, 1995[®]

The He(I) photoelectron spectra of bicyclo[6.1.0]non-1(8)-en-9-one (**1**), bicyclo[8.1.0]undec-1(10)-en-5-yn-11-one (**3**), bicyclo[10.1.0]tridec-1(12)-en-6-yn-13-one (**4**), and bicyclo[12.1.0]pentadec-1(14)-en-7-yn-15-one (**5**) have been investigated. The interpretation is based on the comparison with semiempirical calculations (MINDO/3) and in the case of **3** with ab initio HF-SCF calculations using a 6-31G* basis. The PE investigations reveal a considerable interaction between the triple bond and the cyclopropenone moiety in **3** but only a small or no interaction in **4** and **5**. Our results are substantiated by X-ray investigations on single crystals of **3**. They reveal a boat conformation for the 10-membered ring in the solid state.

Introduction

Medium-sized rings, which incorporate functional groups, are good templates for studying the interaction between groups. Following arguments from perturbation theory,[1] the interaction depends on the resonance integral between both groups (through-space and through-bond) and the difference of their basis orbital energies. Thus, the interaction of groups with the same or very similar basis orbital energies should be the maximum. We assumed that this condition could be met by a combination of a cyclopropenone and a triple bond. By He(I) photoelectron spectroscopy (PE) we found that the vertical π-ionization energy of bicyclo[6.1.0]non-1(8)-en-9-one (**1**) is quite similar to that of cyclooctyne[2] (**2**) (Figure 1). Thus, we supposed that a measurable interaction could be achieved by combining both functions in a suitable framework, providing an overlap of both fragments.

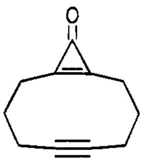
In this paper we report on the He(I) photoelectron (PE) spectroscopic investigations of the first compounds of this type, bicyclo[8.1.0]undec-1(10)-en-5-yn-11-one (**3**), bicyclo[10.1.0]tridec-1(12)-en-6-yn-13-one (**4**), and bicyclo[12.1.0]pentadec-1(14)-en-7-yn-15-one (**5**). All three compounds have been obtained recently[3] via carbene addition to one triple bond of the corresponding cyclic diynes **6**,[4] **7**,[5] and **8**.[5]

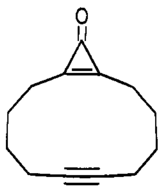

1 2

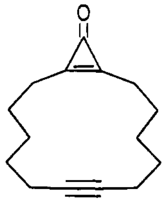
n: 8.56 eV π_1: 9.18 eV

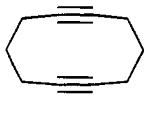
π: 9.67 eV π_2: 9.30 eV

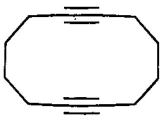
Figure 1. First ionization energies of **1** and **2**.

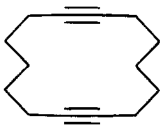

3


4


5


6


7


8

Photoelectron Spectroscopic Studies

The PE spectroscopic investigations of **3**−**5** are of special interest with respect to the electronic structures of cyclodeca-1,6-diyne (**6**), cyclododeca-1,7-diyne (**7**), and cyclotetradeca-1,8-diyne (**8**). The orbital sequences of **6**−**8** have been analyzed by using the concept of the through-space and through-bond interaction.[6] It has been shown[7] that the π/σ and the π/π interactions decrease from **6** to **8**. The strongest effects in **6**−**8** are found for the in-plane π-orbitals π_i, whereas the interactions of the out-of-plane π-orbitals π_o are of minor significance. Consequently, the lack of one π-orbital by

---

[®] Abstract published in *Advance ACS Abstracts,* June 15, 1995.

(1) Heilbronner, E.; Bock, H. *Das HMO-Modell und seine Anwendung*; Verlag Chemie: Weinheim, 1968. Dewar, M. J. S.; Dougherty, R. C. *The PMO Theory of Organic Chemistry*; Plenum Press: New York, 1975.

(2) Bieri, G.; Heilbronner, E.; Kloster-Jensen, E.; Schmelzer, A.; Wirz, J. *Helv. Chim. Acta* **1974**, *57*, 1265.

(3) Gleiter, R.; Merger, M. *Synthesis*, in press.

(4) Gleiter, R.; Karcher, M.; Jahn, R.; Irngartinger, H. *Chem. Ber.* **1988**, *121*, 735.

(5) Gleiter, R.; Merger, R.; Treptow, B.; Wittwer, W.; Pflästerer, G. *Synthesis* **1993**, 558.

(6) Hoffmann, R.; Imamura, A.; Hehre, W. J. *J. Am. Chem. Soc.* **1968**, *90*, 1499. Reviews: Hoffmann, R. *Acc. Chem. Res.* **1971**, *4*, 1. Gleiter, R. *Angew. Chem., Int. Ed. Engl.* **1974**, *13*, 696. Paddon-Row, M. N. *Acc. Chem. Res.* **1982**, *15*, 245. Martin, H. D.; Mayer, B. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 283. Gleiter, R.; Schäfer, W. *Acc. Chem. Res.* **1990**, *23*, 369 and references therein.

(7) Gleiter, R.; Kratz, D.; Schäfer, W.; Schehlmann, V. *J. Am. Chem. Soc.* **1991**, *113*, 9258.

0022-3263/95/1960-4692$09.00/0

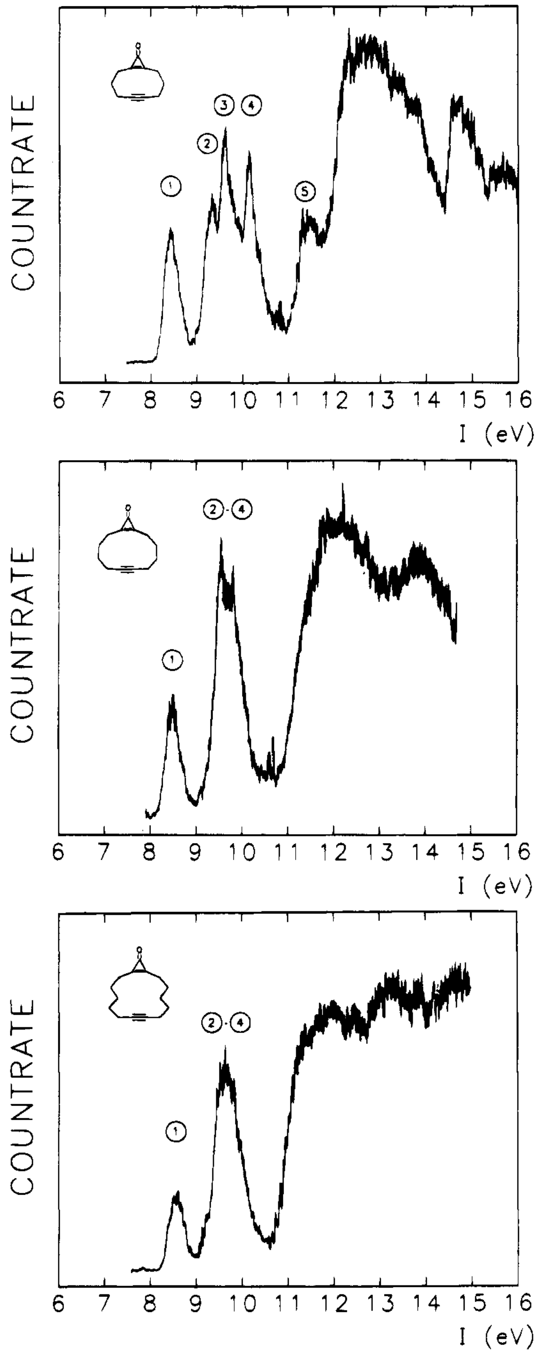


Figure 2. He(I) PE spectra of **3**, **4**, and **5**.

carbene addition to **6**–**8** and the somewhat increasing separations of the π-centers may reduce the interactions.

Indeed, as shown in Figure 2, the PE spectra of **4** and **5** are more characteristic for isolated π-systems with only two distinct features at 8.5 and 9.5–9.8 eV in a ratio of 1:3 (one transition around 8.5 eV, three transitions at 9.5–9.8 eV). However, in contrast, the PE spectrum of **3** exhibits four distinct peaks at 8.42, 9.33, 9.64, and 10.14 eV, each of them representing one transition, apparently indicating a considerable interaction.

To assign the observed bands to different ionic states, we make use of Koopmans' approximation,[8] which allows us to correlate the observed vertical ionization energies with orbital energies ϵ_j of the canonical molecular orbitals (Table 1, columns 3 and 4).

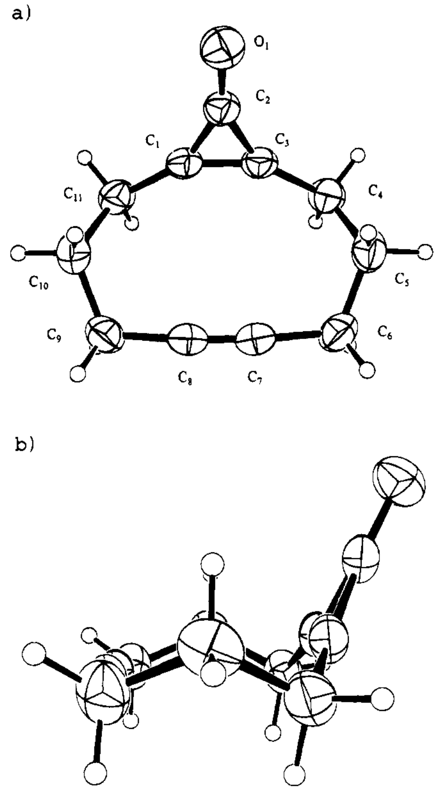


Figure 3. Perspective view of **3**: (a) top view, (b) side view. Thermal ellipsoids are plotted at 50% probability (ORTEP[10]).

By comparison with the data of **1** and **2**, we assign the bands at about 8.5 eV to the "n-orbital" (in fact a $n-\sigma$-combination[9]) at the oxygen of the cyclopropenone and the other bands (three ionization events) to the three "π-orbitals". Taking into account that in **5** there should be no interaction of π-orbitals at all, we can estimate the orbital energies of uninfluenced π-orbitals from its PE spectrum. In the series of **5** to **3**, the range of π-bands increases from about 0.3 to 0.81 eV. A simple interaction of a pair of parallel out-of-plane π-orbitals cannot be responsible for this increase. It even exceeds the interaction of the closer out-of-plane π-orbitals in **6**, which amounts to only about 0.3 eV.

X-ray Investigations on 3

An essential explanation results from the geometrical data of **3**, which were obtained by an X-ray structural analysis (Figure 3, Table 2).

It is remarkable that in **3** a boat conformation with carbons C_5 and C_{10} on the same side (C_s symmetry) is the most stable one, whereas in the case of **6**, a chair conformation is preferred.[4] Due to the bond angle of 148° ($C_1-C_3-C_4$ and $C_3-C_1-C_{11}$) at the cyclopropenone moiety, the transannular distances $C_1 \cdots C_8$ and $C_3 \cdots C_7$ amount to 3.1 Å (**6**: 2.991 Å[4]), and the bond angles at the triple bond are 175.2° and 175.6°, larger than in **6** (171.7°). Thus, the 10-membered ring of compound **3** is less strained than that of **6**. However, enough strain remains to pyramidalize[11] the bridgehead C atoms C_1 and C_3 by 3° and 4.3°.

---

(8) Koopmans, T. *Physica* **1934**, *1*, 104.

(9) Harshbarger, W. R.; Kuebler, N. A.; Robin, M. B. *J. Chem. Phys.* **1974**, *60* (2), 345. Schäfer, W.; Schweig, A.; Maier, G.; Sayrac, T.; Crandall, J. K. *Tetrahedron Lett.* **1974**, 1213.

(10) ORTEP II: Johnson, C. K. *Report ORNL-5138*; Oak Ridge National Laboratory: Oak Ridge, TN 37830, 1976.

(11) Borden, W. T. *Chem. Rev.* **1989**, *89*, 1095.

Table 1. First Ionization Energies $I_{v,j}$ and Calculated Orbital Energies of Compounds 3–5

compd	band	$I_{v,j}$ (eV)	assignment	MINDO/3 (eV)	6-31G* (eV)
3	1	8.42	n_o	−8.64	−9.60
	2	9.33	$\pi_\Delta - \pi_{t,i}$	−9.53	−9.71
	3	9.64	$\pi_{t,o}$	−9.87	−10.17
	4	10.14	$\pi_\Delta + \pi_{t,i}$	−10.09	−10.66
	5	11.4	w	−10.42	−12.94
4	1	8.45	n_o	−8.57	
	2	9.53	$\pi_\Delta - \pi_{t,i}$	−9.78	
	3	to	$\pi_{t,o}$	−9.79	
	4	9.8	$\pi_\Delta + \pi_{t,i}$	−9.85	
	5		w	−10.34	
5	1	8.48	n_o	−8.54	
	2	9.47	$\pi_{t,i}$	−9.71	
	3	to	$\pi_\Delta + \pi_{t,o}$	−9.79	
	4	9.69	$\pi_\Delta - \pi_{t,o}$	−9.81	
	5		w	−10.37	

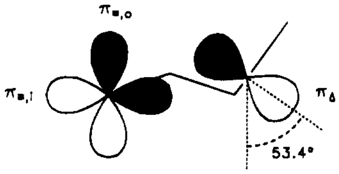


Figure 4. Orientation of the π-orbitals in **3** (schematic).

Table 2. Comparison of Selected Structural Parameters of 3, Resulting from a 6-31G* Calculation with Full Geometry Optimization and an X-ray Investigation

	X-ray	ab initio		X-ray	ab initio
		Distances (Å)			
O_1-C_2	1.221 (2)	1.199	C_6-C_7	1.467 (2)	1.472
C_1-C_2	1.417 (2)	1.409	C_7-C_8	1.191 (2)	1.188
C_1-C_3	1.351 (2)	1.334	C_8-C_9	1.465 (2)	1.472
C_1-C_{11}	1.486 (2)	1.494	C_9-C_{10}	1.528 (2)	1.538
C_2-C_3	1.415 (2)	1.409	$C_{10}-C_{11}$	1.538 (2)	1.545
C_3-C_4	1.489 (2)	1.494	$C_1 \cdots C_8$	3.114 (2)	3.169
C_4-C_5	1.532 (2)	1.545	$C_3 \cdots C_7$	3.117 (2)	3.169
C_5-C_6	1.524 (2)	1.538			
		Bond Angles (deg)			
$O_1-C_2-C_1$	152.1 (1)	151.7	$C_3-C_4-C_5$	111.8 (1)	112.7
$O_1-C_2-C_3$	150.9 (1)	151.7	$C_4-C_5-C_6$	113.7 (1)	114.4
$C_1-C_3-C_2$	61.6 (1)	61.7	$C_5-C_6-C_7$	113.7 (1)	113.2
$C_1-C_3-C_4$	148.4 (1)	148.1	$C_6-C_7-C_8$	175.2 (1)	175.4
$C_1-C_{11}-C_{10}$	112.3 (1)	112.7	$C_7-C_8-C_9$	175.6 (1)	175.4
$C_2-C_1-C_3$	61.4 (1)	61.7	$C_8-C_9-C_{10}$	113.2 (1)	113.2
$C_3-C_2-C_1$	57.0 (1)	56.5	$C_9-C_{10}-C_{11}$	113.8 (1)	114.4
$C_3-C_1-C_{11}$	148.0 (1)	148.1			

Discussion

Concerning the π-interaction, the most important feature of **3** is that the π-orbital of the cyclopropenone ring (π_Δ), together with the carbon atom C_2, moves out of the plane formed by C_1, C_3, C_7, and C_8 by 53.4°, which means that it is not parallel to the out-of-plane π-orbital of the triple bond ($\pi_{t,o}$). It approaches the character of an in-plane orbital and becomes able to interact mainly with the in-plane orbital $\pi_{t,i}$ (Figure 4).

Thus, a linear combination $\pi_\Delta - \pi_{t,i}$ of the in-plane π-orbital of the triple bond and π_Δ results, forming the HOMO-1 (the n-orbital at the oxygen being the HOMO). The out-of-plane π-orbital of the triple bond $\pi_{t,o}$ remains nearly unaffected (HOMO-2), and a linear combination $\pi_\Delta + \pi_{t,i}$ forms the HOMO-3.

Figure 5 summarizes this interpretation; it compares the energies of the π-bands in **5** (small or no interaction) and the assigned π-bands in **3** (interaction of π_Δ and $\pi_{t,i}$). The split by about 0.5 eV is smaller than the split of in-plane orbitals in **6** (1.5 eV) but greater than the split of the out-of-plane orbitals in **6** (0.3 eV).[4]

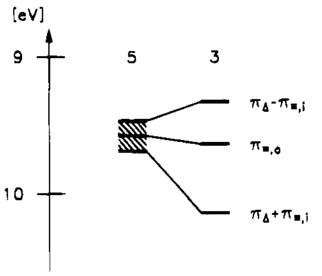


Figure 5. Comparison of π-bands in the PE-spectra of **3** and **5**.

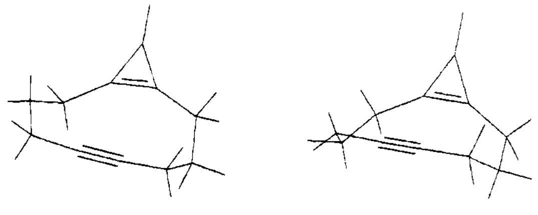

3a **3b**

Figure 6. Two less stable conformations of **3**.

To confirm these conclusions, we carried out semiempirical (MINDO/3)[12] and, in the case of **3** (conformation in the solid state), ab initio (6-31G*, without symmetry restrictions)[13] calculations. The results are listed in Table 1 (columns 5 and 6). The MINDO/3 calculations are in good agreement with the fact that in **3** there is a considerable interaction, but only a small or even no interaction in **4** and **5**. Concerning **3**, the MINDO/3 calculation produces the recorded ionization energies quite satisfactorily, but the resulting difference of $\pi_\Delta - \pi_{t,i}$ and $\pi_\Delta + \pi_{t,i}$ orbital energies (0.5 eV) deviates considerably from the measured value (0.81 eV). In contrast, the 6-31G* calculation, which deviates more from the experimental ionization energies,[14] yields much better data with respect to the split of energies (0.95 eV, Table 1, column 6) and the geometry (Table 2).

Besides the conformer **3** found in the crystal, two additional conformers (**3a,b**, Figure 6) are predicted in the gas phase as local minima by using molecular models. According to ab initio calculations (6-31G*), conformers **3a** and **3b** appear only slightly less stable than **3** (by about 2 and 5 kcal/mol, respectively) and their calculated splits of π-orbitals (0.81 and 0.70 eV) meet the experimental value similarly well as that one of **3**.

In Figure 7, three wave functions (6-31G* basis) of the most stable conformer **3** are shown, indicating a through-space interaction as well as through-bond interactions.

To analyze the through-space and the through-bond interactions[15,16] quantitatively, we used the results obtained by the 6-31G* basis set, since it reproduces the measured interactions best. We transformed[16] the ca-

---

(12) Bingham, R. C.; Dewar, M. J. S.; Lo, D. H. *J. Am. Chem. Soc.* **1975**, *97*, 1285. Bischof, P. *J. Am. Chem. Soc.* **1976**, *98*, 6844.

(13) Frisch, M. J.; Trucks, G. W.; Head-Gordon, M.; Gill, P. M. W.; Wong, M. W.; Foresman, J. B.; Johnson, B. G.; Schlegel, H. B.; Robb, M. A.; Replogle, E. S.; Gomperts, R.; Andres, J. L.; Raghavachari, K.; Binkley, J. S.; Gonzalez, C.; Martin, R. L.; Fox, D. J.; Defrees, D. J.; Baker, J.; Stewart, J. J. P.; Pople, J. A. *Gaussian 92, Revision G.1*; Gaussian, Inc.: Pittsburgh, PA, 1992.

(14) The nonvalidity of Koopmans' theorem for the oxygen "lone pair" ionizations in ketones is well-known; see, e.g.: Lauer, G.; Schäfer, W.; Schweig, A. *Chem. Phys. Lett.* **1975**, *33*, 312. In the MINDO/3 method, this problem is reduced by parametrization.

(15) Heilbronner, E.; Schmelzer, A. *Helv. Chim. Acta* **1975**, *58*, 936. Imamura, A.; Ohsaku, M. *Tetrahedron* **1981**, *37*, 2991.

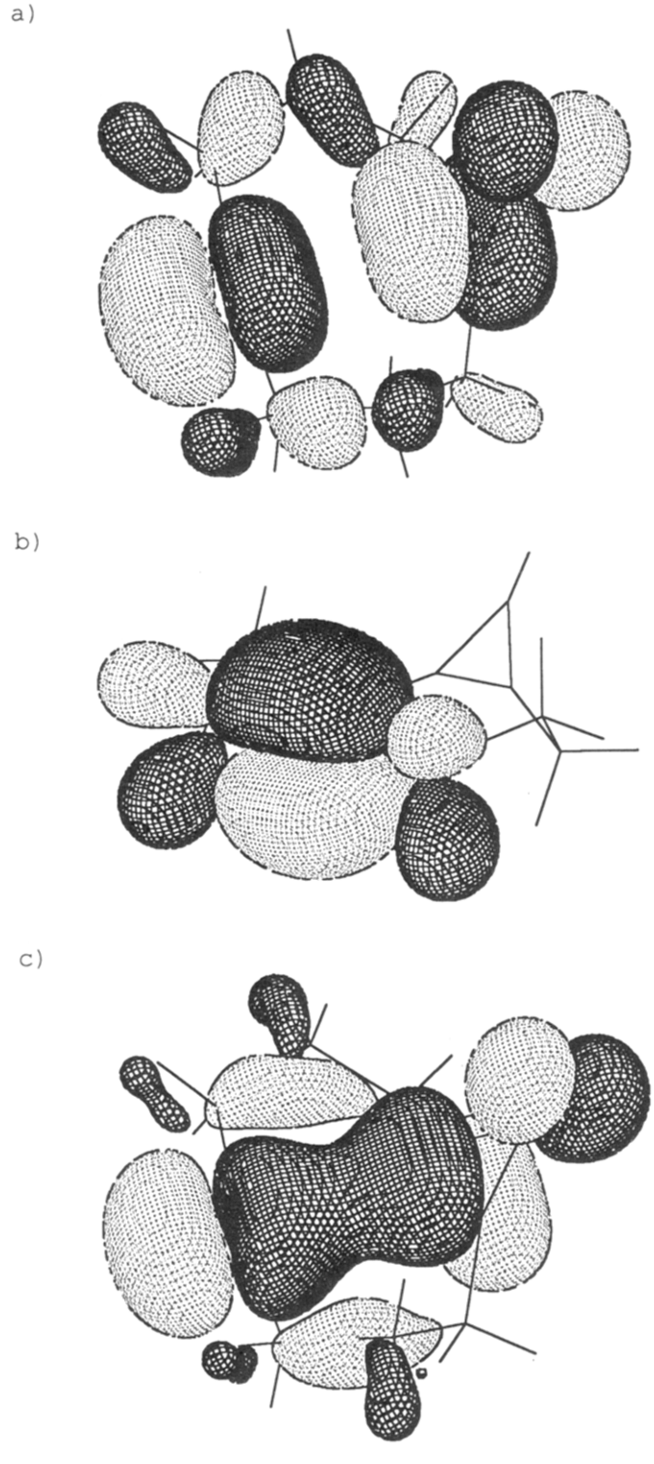


Figure 7. Surfaces of the highest occupied MOs of **3** (6-31G* basis): (a) top view of HOMO-1 ($\pi_\Delta - \pi_{t,i}$); (b) side view of HOMO-2 ($\pi_{t,o}$); (c) top view of HOMO-3 ($\pi_\Delta + \pi_{t,i}$). Value = 0.032.

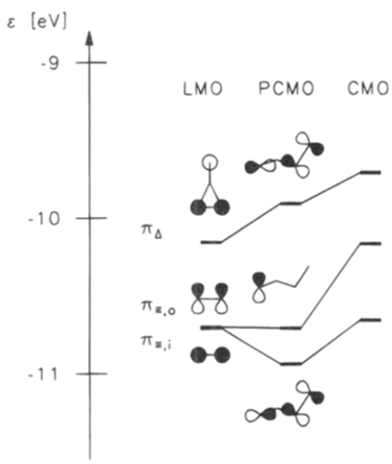


Figure 8. Localized, precanonical, and canonical π MOs in **3**, calculated with GAUSSIAN92 and G92NBO (6-31G* basis set).

nonical molecular orbitals (CMOs) φ_j of **3** into a set of natural bond orbitals (NBOs) λ_j by means of the Weinhold NBO localization procedure.[17] This led to localized π- and π^*-orbitals $\lambda_6 \equiv \pi_{t,o}$, $\lambda_7 \equiv \pi_{t,i}$, $\lambda_{27} \equiv \pi_{C=O}$, $\lambda_{29} \equiv \pi_d$, and $\lambda_{202} \equiv \pi^*_{C=O}$.[18]

We first had to consider the π-interactions within the cyclopropenone moiety: There is a destabilizing effect by an antibonding interaction between the double bond of the three-membered ring, π_d, and the $\pi_{C=O}$ MOs and a stabilizing effect on the double bond by a bonding interaction between the π_d and the $\pi^*_{C=O}$ MO.[9] This leads to a π-combination $\pi_\Delta = \pi_d - \pi_{C=O} + \pi^*_{C=O}$ with an energy of −10.16 eV (Figure 8), so that the energy gap between the π_Δ and π_t ($F_{\lambda,6} = F_{\lambda,7} = -10.71$ eV) orbitals is only 0.55 eV (Figure 8, LMO). Thus, π_Δ and $\pi_{t,i}$ are enabled to interact through space, which leads to the PCMOs in Figure 8. The out-of-plane orbital $\pi_{t,o}$ remains nearly unaffected at −10.71 eV, whereas the $\pi_{t,i}$ and the π_Δ orbitals split into an antibonding combination at −9.91 eV and a bonding combination 1.03 eV below. In this way the gap rises by 0.48 eV.

Since the π^*_t-orbitals do not have an effect on the π-orbitals, the difference in energies of those PCMOs, taking only through-space interactions into account, and the canonical molecular orbitals (Figure 8, CMO) yields the through-bond interaction. The split, caused by the through-space interaction, is diminished by the through-bond interaction by 0.08 eV: The antibonding $\pi_\Delta - \pi_{t,i}$ combination is raised a little less than the bonding $\pi_\Delta + \pi_{t,i}$ combination. The overall energy gap sums up to 0.95 eV.

Considering the good agreement of experimental and calculated data, it finally seemed reasonable to study the consequences of shortening the distance between the π-functions in a lower homologue of **3**, employing the same calculating methods. We performed an ab initio calculation (6-31G*, without symmetry restrictions)[13] on the hitherto unknown bicyclo[6.1.0]non-1(8)-en-4-yn-9-one (**9**) (Figure 9).

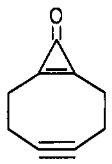
According to this calculation, **9** is predicted to have C_2 symmetry. Contrary to **3**, in **9** the "in-plane" π-orbital $\pi_{t,i}$ is uneffected by the cyclopropenone, whereas the "out-

---

(16) Glendening, E. D.; Reed, A. E.; Carpenter, J. E.; Weinhold, F. *G92NBO, Version 3.1*; Theoret. Chem. Inst. and Department of Chemistry, University of Wisconsin: Madison, WI 53706. Paddon-Row, M. N.; Jordan, K. D. in *Modern Models of Bonding and Delocalization*; Liebman, J. F., Greenberg, A., Eds.; Verlag Chemie: Weinheim, 1988; p 115. Martin, H.-D.; Mayer, B. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 283. Gleiter, R.; Schäfer, W. *Acc. Chem. Res.* **1990**, *23*, 369.

(17) Foster, J. P.; Weinhold, F. *J. Am. Chem. Soc.* **1980**, *102*, 7211. Reed, A. E.; Weinstock, R. B.; Weinhold, F. *J. Chem. Phys.* **1985**, *83*, 735. Reed, A. E.; Weinhold, F. *J. Chem. Phys.* **1985**, *83*, 1736. Carpenter, J. E.; Weinhold, F. *J. Am. Chem. Soc.* **1988**, *110*, 368. Reed, A. E.; Weinhold, F. *QCPE Bull.* **1985**, *5*, 141.

(18) Self-energies of the localized π orbitals: $F_{\lambda,6} = -10.71$ eV ($\pi_{t,o}$), $F_{\lambda,7} = -10.71$ eV ($\pi_{t,i}$), $F_{\lambda,27} = -13.48$ eV ($\pi_{C=O}$), $F_{\lambda,29} = -8.75$ eV ($\pi_=$), $F_{\lambda,202} = +6.14$ eV ($\pi^*_{C=O}$).



9

orbital	6-31G* [eV]
n	**- 9.79**
π_Δ-π_o	**- 10.12**
π_i	**- 10.33**
π_Δ+π_o	**- 10.68**

Figure 9. Calculated orbital energies of **9** (6-31G* basis set).

of-plane" π-orbital $\pi_{t,o}$ interacts with the π_Δ-orbital of the three-membered ring. This leads to orbitals $\pi_\Delta - \pi_{t,o}$ (HOMO-1, −10.12 eV), $\pi_{t,i}$ (HOMO-2, −10.33 eV), and $\pi_\Delta + \pi_{t,o}$ (HOMO-3, −10.68 eV). $\pi_\Delta - \pi_{t,o}$ and $\pi_\Delta + \pi_{t,o}$ differ by 0.56 eV (Figure 9), which is less than the gap between $\pi_\Delta - \pi_{t,i}$ and $\pi_\Delta + \pi_{t,i}$ in **3**, although the π-centers are closer (2.78 Å calculated for **9**, 3.11 Å found in **3**). This could be a consequence of the orientation of the π-orbitals or of a σ-effect, diminishing the split due to through-space interaction.

NBO localization (6-31G* basis set) and evaluation of submatrices of the NBO Fock matrix states that the through-space interaction (0.13 eV) indeed is smaller than it is in **3**, and the overall split is the result of this weak through-space and an additional, larger through-bond interaction.

Conclusions

We have shown that bicyclo[8.1.0]undec-1(10)-en-5-yn-11-one (**3**) adopts a boat conformation for the 10-membered ring in the solid state. The data obtained from the X-ray analysis indicate a considerable strain in the system. The PE data demonstrate a strong interaction between the π-system of the triple bond and the cyclopropenone unit in **3**. We ascribe this mainly to a favourable conformation in the 10-membered ring. In the case of **4** and **5**, the interaction between the triple bond and the cyclopropenone π-system must be small.

Experimental Section

He(I) PE spectra were recorded on a Perkin-Elmer, PS18, calibration with Ar and Xe, 0.2 meV resolution on the $^2P_{3/2}$ line of Ar. X-ray structure analysis of **3**: The compound was crystallized from cyclohexane at ambient temperature. The X-ray data were collected at 293 K on an automated diffractometer (Enraf-Nonius CAD4, graphite monochromator, Mo Kα radiation, $\omega - 2\theta$ scan). Intensities were corrected for Lorentz and polarization effects. The structure was solved by direct methods (MULTAN[19]). Refinements on F^2 were carried out by full-matrix least-squares procedures with anisotropic thermal parameters for the carbon and oxygen atoms. The MolEN program system[20] was used for crystallographic calculations.[21]

Acknowledgment. We are grateful to A. Flatow for recording the PE spectra. We thank the Deutsche Forschungsgemeinschaft (SFB 247), the Fonds der Chemischen Industrie, and the BASF Aktiengesellschaft (Ludwigshafen) for financial support. M. Merger thanks the Studienstiftung des Deutschen Volkes for a graduate fellowship.

JO950162R

---

(19) Main, P.; Fiske, S. J.; Hull, S. E.; Lessinger, L.; Germain, G.; Declercq, J.-P.; Woolfson, M. M. *MULTAN 11/82*; Department of Physics, University of York: York, England, 1982.

(20) *MolEN: Structure Determination System*; Enraf-Nonius, Delft Instruments X-RAY Diffraction B.V.: Delft, Netherlands, 1990.

(21) The authors have deposited tables of crystallographic refinement parameters, atomic coordinates, and the thermal parameters of **3** with the Cambridge Crystallographic Data Centre. The coordinates can be obtained, on request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK.