Synthesis and PE Spectra of 1-Ethynyl- and 1,4-Diethynylbicyclo[2.2.2]octane, and of Related 1,4-Dihalobicyclo[2.2.2]octanes[1]

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Received July 21, 1986

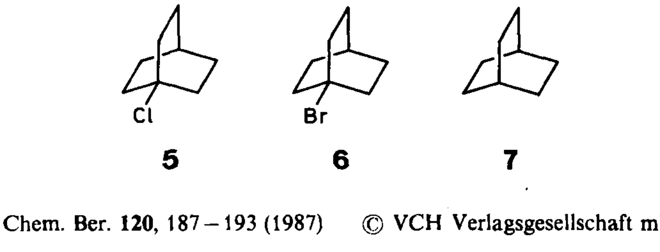
The synthesis of 1-ethynylbicyclo[2.2.2]octane (**1**), of 1,4-diethynylbicyclo[2.2.2]octane (**2**), of 1,4-dichloro- (**3**) and of 1,4-dibromobicyclo[2.2.2]octane (**4**) is reported. The He(Iα) photoelectron spectra of **1** and **2** have been assigned using the STO-3G and the HAM/3 procedure, whereas those of **3** and **4** have been interpreted on the basis of an equivalent bond orbital model including spin-orbit coupling.

Synthese und PE-Spektren von 1-Ethinyl- und 1,4-Diethinylbicyclo[2.2.2]octan und verwandten 1,4-Dihalobicyclo[2.2.2]octanen[1]

Die Synthese von 1-Ethinylbicyclo[2.2.2]octan (**1**) und 1,4-Diethinylbicyclo[2.2.2]octan (**2**), von 1,4-Dichlor- (**3**) und von 1,4-Dibrombicyclo[2.2.2]octan (**4**) wird beschrieben. Die He(Iα) Photoelektronenspektren von **1** und **2** wurden mit Hilfe von STO-3G- und HAM/3-Rechnungen zugeordnet, während für die Deutung der Spektren von **3** und **4** ein Modell äquivalenter Bindungsorbitale verwendet wurde, welches die Spin-Bahn-Kopplung berücksichtigt.

The assignment of the PE spectra of 1-substituted and of 1,4-disubstituted bicyclo[2.2.2]octanes or related cage-molecules can present serious difficulties, which have to be kept in mind when attempting a rationalization of such an assignment in terms of qualitative concepts. As long as the molecules consist only of first and second row atoms, the usual ab initio or semiempirical models provide a rather safe basis as we shall see by discussing in detail the PE spectra of 1-ethynylbicyclo[2.2.2]octane (**1**) and of 1,4-diethynylbicyclo[2.2.2]octane (**2**). However, the problem becomes more involved when the substituents are heavy atoms, e.g., halogen atoms. Thus a recent investigation of the He(Iα) PE spectra of symmetrical 1,4-dihalonorbonanes[2] has shown that the assignment of such spectra is anything but straightforward. Extensive mixing between the substituent and parent-molecule orbitals does no longer allow a unique classification of the observed PE bands as e.g. dominantly n_p^{-1} or σ^{-1} bands.

Scheme 1



In addition, spin-orbit coupling becomes an important factor which has to be considered. To this end we use a simple equivalent bond orbital treatment[3], implemented to take care of spin-orbit coupling[2], which we apply to 1,4-dichloro- (**3**), 1,4-dibromo- (**4**), 1-chloro- (**5**), and 1-bromobicyclo[2.2.2]octane (**6**).

Experimental Results

PE Spectra

The He(Iα) PE spectra of **1** – **6** are shown in Figures 1 – 3. The numbering of the bands relies on the assignment proposed below and the corresponding positions. I_j^m values of the band maxima are listed in Tables 1 and 2. It is assumed that the I_j^m values are close to the vertical ionisation energies I_j^v. The PE spectrum of **6** has already been recorded and discussed by Della et al.[4]. Their I_j^m values are included in Table 2. Finally, the PE spectrum of the parent hydrocarbon bicyclo[2.2.2]octane (**7**) can be found in ref.[5].

Syntheses

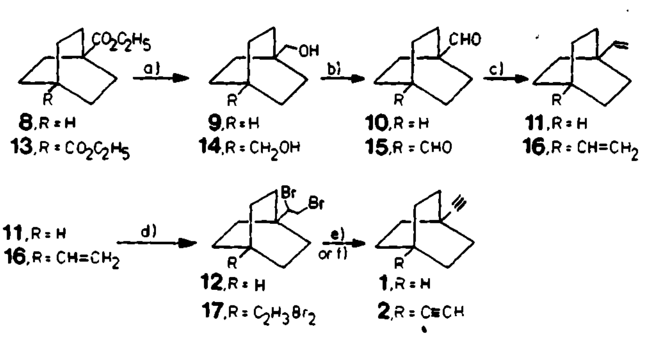
Ethyl bicyclo[2.2.2]octane-1-carboxylate (**8**) was reduced to 1-(hydroxymethyl)bicyclo[2.2.2]octane (**9**)[6], which was converted into the corresponding carboxaldehyde **10** by Swern oxidation with oxalyl chloride, dimethyl sulfoxide, and triethylamine. Wittig reaction of **10** with triphenylphosphonium methylide provided 1-vinylbicyclo[2.2.2]octane (**11**), which was brominated at room temperature to form the dibromide **12**. Subsequent dehydrobromination of **12** by refluxing it with excess potassium hydroxide in dry ethanol yielded **1** as a volatile liquid.

The corresponding 1,4-diethynyl derivative **2** was prepared in analogy to the procedure described above: According to Sukenik[7] et al. diethyl bicyclo[2.2.2]octane-1,4-

Chem. Ber. **120**, 187 – 193 (1987) © VCH Verlagsgesellschaft mbH, D-6940 Weinheim, 1987 0009 – 2940/87/0202 – 0187 $ 02.50/0

dicarboxylate (**13**)[8] was reduced by lithium aluminium hydride in dry diethyl ether to form the bisalcohol **14**, which was oxidized with oxalyl chloride, DMSO, and triethylamine. The bicyclo[2.2.2]octane-1,4-dicarboxaldehyde (**15**) reacted with methyltriphenylphosphonium iodide in the presence of excess *n*-butyllithium (*n*-hexane) to provide 1,4-divinylbicyclo[2.2.2]octane (**16**) in moderate yield. By stirring with bromine at room temperature the diene **16** was converted into the tetrabromide **17**, which appeared in form of two different solid fractions, probably diastereomeres. Complete dehydrobromination of **17** took place when it was refluxed with excess potassium hydroxide in dry ethanol/dioxane (2:1). Thus, 1,4-diethynylbicyclo[2.2.2]octane (**2**) was formed as a colourless, crystalline solid.

Scheme 2



Reaction conditions:

a) Refluxing with lithium aluminium hydride in dry diethyl ether for 5−7 h, hydrolysis with KOH/methanol.

b) 1) Oxalyl chloride in dry CH_2Cl_2, −70°C; 2) DMSO in dry CH_2Cl_2, −70°C; 3) triethylamine, −30°C; 4) H_2O, room temperature.

c) Methyltriphenylphosphonium iodide in dry THF + *n*-butyllithium in *n*-hexane, −5°C; 18 h stirring at room temperature.

d) Stirring with excess bromine in CH_2Cl_2 or CCl_4 for 8−10 h at room temperature.

e) Refluxing with excess KOH in dry ethanol for 10 h.

f) Refluxing with excess KOH in dry ethanol/dioxane (2:1) for 10 h.

Discussion of the PE Spectra

1-Ethynylbicyclo[2.2.2]octane (1), 1,4-Diethynylbicyclo[2.2.2]octane (2)

At first sight, the task of assigning the PE spectra of **1** and **2** looks rather straightforward, because of the seemingly well structured band systems. Ones first tendency would be to associate band (2) of **1** and band (3) of **2** with electron ejection from the degenerate molecular orbitals dominated by the triple bond π orbitals $\pi_{1,+}$, $\pi_{1,-}$ in **1** or $\pi_{1,+}$, $\pi_{1,-}$, $\pi_{4,+}$, $\pi_{4,-}$ in **2** because of the prominent vibrational fine structure with spacings of approx. 1600 cm^{-1} (for **1**) and 1900 cm^{-1} (for **2**). Such values are typical for π^{-1} bands in the PE spectra of acetylene derivatives[9]. However, the positions I_2^m = 10.35 eV of band (2) of **1** and I_3^m = 10.85 eV of band (3) in **2** are completely incompatible with such an interpretation, and are thus a clear indication that these bands can not be due to a π^{-1} ionization process.

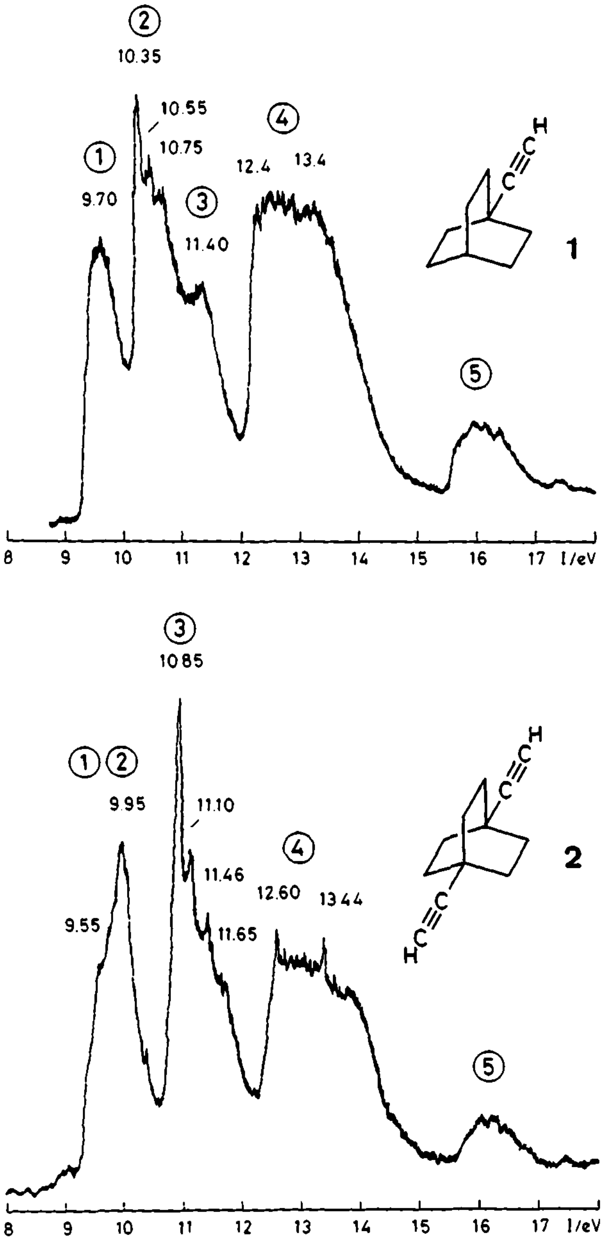


Fig. 1. He(Iα) PE spectra of **1** and **2**

If the bicyclo[2.2.2]octyl group is treated as one of the alkyl substituents R in the series of alkylacetylenes R−C≡CH, R = Me, Et, etc.[10], the usual LFER type treatment[11] may be applied to predict the position of the π^{-1} band. The necessary shift parameters[12] can be derived from the PE spectroscopic results of a variety of alkyl-substituted target groups X, e.g. the alkyl halides RX[12−14], the alcohols ROH[15], alkyl-substituted ethenes $RCH=CH_2$[16], in combination with those of the alkylacetylenes[10], which allow an extrapolation to **1**. The expectation value obtained for **1** in this fashion is I^m (π^{-1}) = 9.6 eV, give or take 0.1 to 0.2 eV, which excludes the assignment of band (2) to this ionization process, notwithstanding its "distinctive" vibrational fine-structure.

Under these conditions, a tentative assignment has to rely on model calculations. From previous experience the most

Table 1. Assignment of the PE spectra of **1** and **2** according to the ab initio STO-3G ($\varepsilon_j^{\text{STO-3G}}$) and the HAM/3 ($\varepsilon_j^{\text{HAM/3}}$) model. The values $\varepsilon_j^{\text{calib.}}$ have been calculated from the $\varepsilon_j^{\text{STO-3G}}$ values according to:

$$\varepsilon_j^{\text{calib.}} = -1.905\ \text{eV} + 0.821\ \varepsilon_j^{\text{STO-3G}}.$$

Note the reversal of $1a_1''$ and $6a_1'$ (a) and of $2e''$ and $3e'$ (b) in the computed sequence from the HAM/3 model vs. the STO-3G model

1-Ethynylbicyclo[2.2.2]octane (**1**)

C_{3v} Orb.	$-\varepsilon_j^{\text{STO-3G}}$/eV	$-\varepsilon_j^{\text{calib.}}$/eV	$-\varepsilon_j^{\text{HAM/3}}$/eV	I_j^m/eV
8e	8.52	8.90	9.45	9.70
7e	10.32	10.38	10.53	10.35
$9a_1$	10.56	10.57	10.76	
$2a_2$	11.45	11.31	11.26	11.4
6e	12.70	12.33	11.86	12.4
5e	13.12	12.68	12.81	
4e	13.43	12.93	12.95	
$8a_1$	13.65	13.11	13.56	
$1a_2$	14.40	13.73	14.01	14

1,4-Diethynylbicyclo[2.2.2]octane (**2**)

D_{3h} Orb.	$-\varepsilon_j^{\text{STO-3G}}$/eV	$-\varepsilon_j^{\text{calib.}}$/eV	$-\varepsilon_j^{\text{HAM/3}}$/eV	I_j^m/eV
$4e''$	8.56	8.93	9.35	9.60
$5e'$	8.73	9.07	9.47	9.95
$3e''$	10.82	10.79	10.66	10.85
$6a_1'$	11.05	10.98	11.29[a]	
$1a_1''$	11.63	11.45	11.25[a]	11.65
$4e'$	13.14	12.69	12.01	12.60
$3e'$	13.28	12.81	12.90[b]	
$2e''$	13.66	13.12	12.83[b]	14.5

Table 2. Ionization energies I_j^m/eV of the molecules **3** to **6**. The probable error is ±0.02 eV if a second decimal is given, ±0.05 eV if the second decimal is given as a subscript, or ±0.1 eV if only one decimal is given. S.O. = Split due to spin-orbit coupling

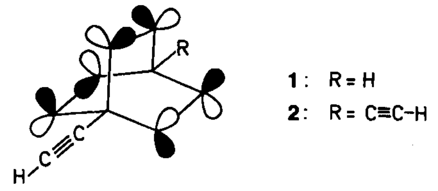
Band	3	4	5	6 a)	6 b)
1		9.94		9.68	9.67
		S.O.	10.4	S.O.	S.O.
		10.06		9.97	9.96
		S.O.			
		10.21			
2	10.7			10.4	10.39
		10.38	10.8_5		
3		10.8_5		10.7_5	10.7
4			11.6_5	11.6_0	11.6
	11.6	11.9			
5					

a) This work. – b) From reference[4].

reliable orbital treatments for hydrocarbons such as **1** or **2** are the ab initio STO-3G procedure[17] and the highly parametrized HAM/3 model[18]. As shown in Table 1, both treatments yield the same orbital sequence, with only a minor reversal of the orbitals $6a_1'$, $1a_1''$ and $3e'$, $2e''$ of **2**. As is usual for the STO-3G model, the triple bond orbitals are calculated to lie too high with respect to the σ orbitals, a defect which can not be entirely corrected by using a calibration function (cf. Table 1). Apart from these defects, the over-all agreement between the computed orbital energies and the observed band pattern is satisfactory and it is believed that the assignment presented in Table 1 is at least a reasonable one.

A tentative, but plausible explanation of the vibrational fine-structure observed for the composite bands (2) of **1** and (3) of **2** rests on the following arguments. Both these molecules possess a MO which, for symmetry reasons, is completely and uniquely localized on the methylenic CH bonds, namely $2a_2$ of **1** and $1a_1''$ of **2**, as shown in Scheme 3.

Scheme 3



Whereas $2a_2$ is well separated in energy from the low-lying MO $1a_2$ of same symmetry in **1**, the MO $1a_1''$ is indeed the only one of its type in **2**. It has already been observed in other rigid cage molecules, e.g. in cubane[19] or in pentaprismane[20], that electron ejection from such CH-centered MOs leads to bands in the PE spectrum with well resolved vibrational fine-structure. In the present case this fine-structure rides on the background provided by the broad bands due to $7e^{-1}$ and $9a_1^{-1}$ or the $3e''^{-1}$ and $6a_1'^{-1}$ ionizations, respectively, thus leading to structures reminiscent of the traditional π^{-1} bands in acetylene derivatives.

An alternative rationalization based on the theoretical results presented in Table 1 would be to assign band (2) of **1** to orbital 7e and band (3) of **2** to $3e''$, both of which are also strongly localized on the bicyclo[2.2.2]octane moiety. However, it is less likely that electron ejection from degenerate orbitals, which could lead to a Jahn-Teller distortion, would result in such a well defined vibrational fine-structure.

1,4-Dihalo- and 1-Halobicyclo[2.2.2]octanes (3–6)

Application of the equivalent bond orbital model[3], adapted to halogen-substituted molecules of type **3** to **6** by the inclusion of the appropriate terms taking into account spin-orbit coupling[2], leads to the orbital energies and to the orbital sequence listed in Table 3. The numbering of the symmetry labels of the individual canonical molecular orbitals φ_j takes only the valence shell orbitals into account, i.e. it disregards the carbon ls orbitals as well as the inner orbitals of the halogen atoms. The correlation with the I_j^m values of the individual bands in the PE spectra (cf. Figs. 2 and 3) corresponds to the assignments proposed on the basis of the above calculations.

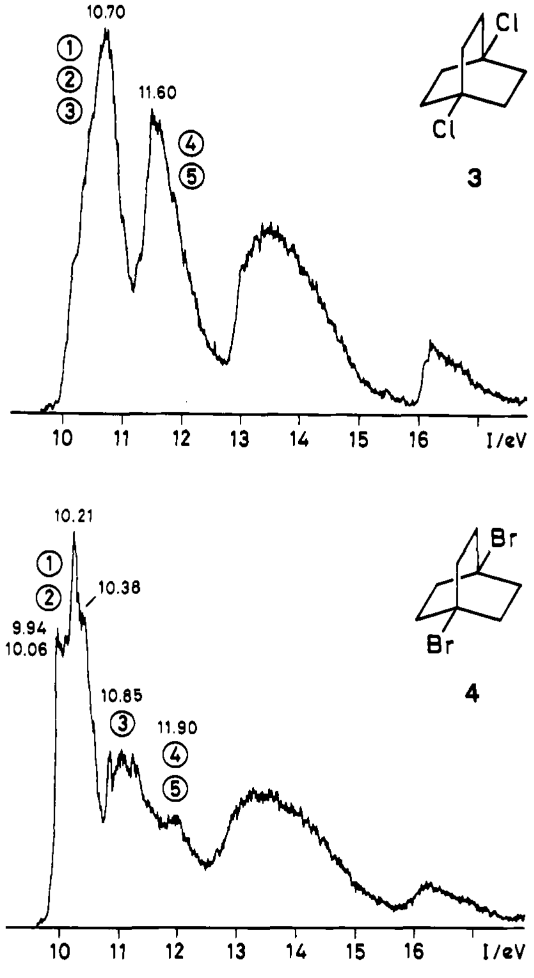


Fig. 2. He(Iα) PE spectra of 3 and 4

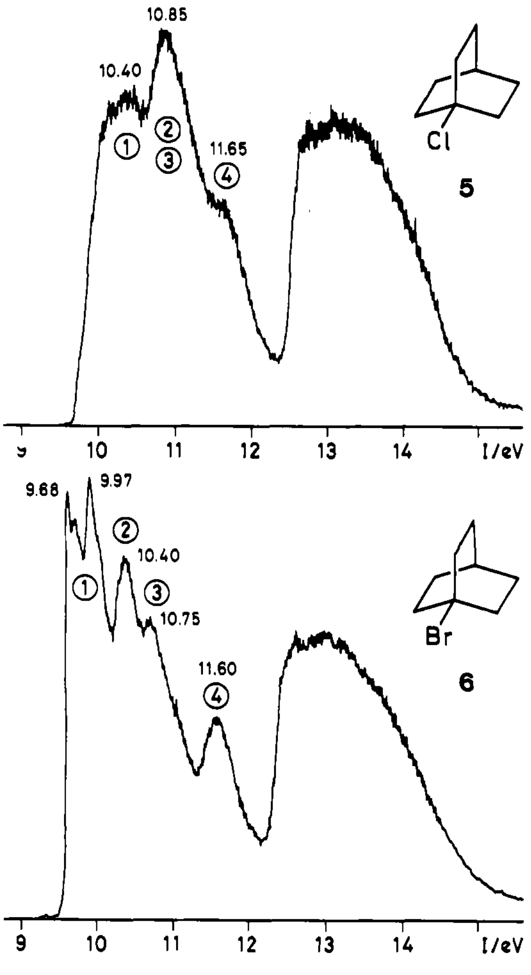


Fig. 3. He(Iα) PE spectra of 5 and 6

Remarks

3: Electron ejection from one of the orbitals $\varphi_j = 4e''$, $5e'$ and $4a_1'$ gives rise to the bands (1), (2), and (3), respectively, which overlap to yield the band system around 10.7 eV. Both $4e''$ and $5e'$ could be classified as lone pair orbitals, albeit considerably mixed with orbitals of the bicyclo[2.2.2]octane moiety (cf. Table 3). On the other hand, orbital $4a_1'$ is heavily centered on the CCl σ bonds. The second band system, with its maximum at 11.60 eV and containing bands (4) and (5), is due to electron ejection from the orbitals $3e''$ and $1a_1''$. Orbital $3e''$ shows a dominant contribution from the chlorine lone-pair orbitals 3p(Cl), whereas the orbital $1a_1''$ is exclusively located on the CH bonds, and therefore only marginally affected by the chlorine substituents in positions 1 and 4.

4: The low energy band system around 10.2 eV has to be correlated with electron ejection from the nearly degenerate orbitals $4e''$ and $5e'$. Because of the larger spin-orbit coupling coefficient of the Br atoms, this band system is much more structured than in the case of **3**. Also the contribution of the 4p(Br) basis orbitals is more important since their self energies lie well above those of the 3p(Cl) orbitals in **3**. Band (3) with its maximum at 10.8_5 eV is assigned to removal of an electron from the orbital $4a_1'$, which is again located to about 50 percent on the CBr σ bonds. Finally, electron ejection from the orbitals $1a_1''$ and $3e''$ gives rise to the overlapping bands (4) and (5) with their joint maximum at 11.9 eV.

5: Band (1) with its maximum at 10.4 eV corresponds to the ejection of the electrons from the orbitals 8e, which exhibit approx. 25 percent contribution from the chlorine lone-pair orbitals 3p(Cl). Bands (2) and (3), associated with the ejection of electrons from the orbitals $7a_1$ and 7e, give rise to the band system with its maximum at 10.8_5 eV. The orbitals 7e show larger contributions from the chlorine lone-pair orbitals than the higher lying orbitals 8e. The shoulder at 11.6_5 eV is assigned to an ionization process where the electron is ejected from orbital $2a_2$, which is entirely located at the CH bonds and therefore corresponds to the orbital $1a_1''$ in the case of the 1,4-disubstituted bicyclo[2.2.2]octanes **3** and **4**.

6: The first band (1) is again ascribed to ejection of electrons from the orbitals 8e. It is split by 0.29 eV because of spin-orbit coupling. The first component with its maximum of 9.68 eV exhibits a vibrational fine-structure ($\tilde{\nu} \approx 726$ cm^{-1}). This suggests a considerable contribution from the bromine lone-pair orbitals 4p(Br), and this is confirmed by the EBO model. Band (2) with its maximum at 10.4 eV is due to ejection of an electron from the orbital $7a_1$, to which bond-orbital λ_{CBr} contributes about 23 percent. Band

Table 3. Orbital energies ε_j (including spin-orbit coupling) and orbital labels of the molecular orbitals φ_j (disregarding spin-orbit coupling) derived from an Equivalent Bond-Orbital (EBO) model[2,3]. The values given in the column "percentage" are 100 times the squares of the coefficients of the halogen atom np orbitals ($3p_+$, $3p_-$ or 4_{p+}, $4p_-$ of Cl or Br, respectively) or of the carbon-halogen atom σ bond orbitals λ_{CX}

3

		Percentage			
$-\varepsilon_j$/eV	φ_j	3p(Cl)	λ_{CCl}	I_j^a/eV	
10.47	4e"	37	–		
10.49		36	–		
11.13	$4a_1$'	–	47	10.7	
11.27	5e'	65	–		
11.31		64	–		
12.37	$1a_1$"	–	–	11.6	
12.99	3e"	40	–		
13.02		40	–		
13.31	$3a_2$"	–	72		

4

		Percentage			
$-\varepsilon_j$/eV	φ_j	4p(Br)	λ_{CBr}	I_j^a/eV	
9.81	4e"	45	–	9.94	S.O.
9.94		40	–	10.21	
10.45	5e'	71	–	10.06	S.O.
10.67		67	–	10.38	
10.68	$4a_1$'	–	48	10.8_5	
11.97	$1a_1$"	–	–	11.9	
12.30	3e"	41	–		
12.43		44	–		
12.66	$3a_2$"	–	78		

5

		Percentage			
$-\varepsilon_j$/eV	φ_j	3p(Cl)	λ_{CCl}	I_j^a/eV	
10.51	8e	25	–	10.4	
10.52		23	–		
10.92	$7a_1$	–	18	10.8_5	
11.64	7e	34	–		
11.66		35	–		
12.03	$2a_2$	–	–	11.6_5	

6

		Percentage			
$-\varepsilon_j$/eV	φ_j	4p(Br)	λ_{CBr}	I_j^a/eV	
9.99	8e	44	–	9.68	S.O.
10.11		37	–	9.97	
10.68	$7a_1$	–	23	10.4	
11.32	7e	26	–	10.7_5	
11.40		28	–		
11.86	$2a_2$	–	–	11.6_0	

(3) corresponds to the orbitals 7e which are not as much localized on the Br atom as orbital 8e in contrast to the situation observed for **5**. The sharp band (4) at 11.6_0 eV is assigned to loss of an electron from orbital $2a_2$.

This work was supported by the *Schweizerischer Nationalfonds zur Förderung der Wissenschaften*[1]. Support by *Ciba-Geigy S. A., F. Hoffmann-LaRoche & Cie. S. A.*, and by *Sandoz S. A.* (Basel) is gratefully acknowledged. We also appreciate support by the *Fonds der Chemischen Industrie*, the *Dr. Jost-Henkel-Stiftung*, and the *BASF Aktiengesellschaft*.

Experimental

Melting points are uncorrected. – Solvents: Dichloromethane was distilled over P_4O_{10}. Dibromoethane and diiodomethane were distilled over calcium oxide directly before use. Benzene, DMF, DMSO, dioxane, diethyl ether, pentane, and THF were dried by refluxing and subsequent destillation over calcium hydride. – The Swern oxidation, the Wittig reaction, and the preparation of the bridgehead halogen derivatives were performed under nitrogen. All samples were stored under nitrogen and to the exclusion of light; their purity was checked by VPC on several columns.

^{1}H-NMR spectra: Varian EM 360 A, 60 MHz. – ^{13}C-NMR spectra: Varian XL 100, 25.2 MHz. – IR spectra: Perkin-Elmer 710 B. – Photoelectron spectra: Leybold-Heraeus UPG 200 or home-built spectrometer, University of Basel. – Preparative VPC: Perkin-Elmer F 22.

Bicyclo[2.2.2]octane-1-carboxaldehyde (**10**): Oxalyl chloride (1.8 g, 13 mmol) in 35 ml of anhydrous dichloromethane was cooled to –70°C; DMSO (2.3 g, 30 mmol) in 30 ml of CH_2Cl_2 was added. The mixture was stirred for 30 min at that temperature, before the alcohol **9**[6] (1.8 g, 13 mmol) in 20 ml of CH_2Cl_2 and 1 ml of DMSO was added dropwise. During 3 h the mixture was warmed to –30°C. Triethylamine (5.1 g, 52 mmol) was added; the temperature raised to 0°C during one hour. The reaction was quenched with 60 ml of water. The organic layer was separated, washed with water, treated with active charcoal, and dried over sodium sulfate. The solvent was removed under reduced pressure. The remainder was distilled in a Büchi "Kugelrohr" apparatus at 90°C/0.1 Torr to provide **10** (1.7 g, 93%) as a low melting solid being stored at –10°C. – IR (film): 3400 (C=O), 2920, 2895, 2840, 2780, 2670, 2640 (CH), 1705 cm^{-1} (C=O). – ^{1}H NMR ($CDCl_3$/TMS): δ = 1.63 (s, 13H), 9.42 (s, 1H). – ^{13}C NMR ($CDCl_3$/TMS): δ = 24.54 (d, $^1J_{C,H}$ = 136 Hz), 24.92 + 25.37 (2 t, $^1J_{C,H}$ = 131 Hz), 42.91 (s/"d", $^2J_{C,H}$ = 21 Hz), 205.91 (d, $^1J_{C,H}$ = 166 Hz). – GC-MS (70 eV): m/z = 138 (18%, M^+), 109 (100, $[C_8H_{13}]^+$).

1-Vinylbicyclo[2.2.2]octane (**11**): The carboxaldehyde **10** (3.1 g, 22 mmol) in 20 ml of anhydrous THF was dropped at –5°C to a

THF solution of methyltriphenylphosphonium iodide (11 g, 27 mmol) which had been converted into the ylide by means of excess *n*-butyllithium in *n*-hexane. The reaction mixture was stirred at room temperature for 18 h. After dilution with dry diethyl ether triphenylphosphane oxide precipitated. The mixture was filtrated, the solvents were evaporated, and the remainder was treated with dry pentane. Again triphenylphosphane oxide could be separated by filtration with the help of Celite (EGA-Chemie). After removal of the solvents the crude product was purified by distillation in a "Kugelrohr" apparatus at 150 °C/15 Torr to provide **11** (1.5 g, 50%) as a colourless liquid. – IR (film): 3075, 3055 (=CH), 2995, 2930, 2910, 2855 (CH), 1630 cm^{-1} (C=C). – ^{1}H NMR (CDCl$_3$/TMS): $\delta = 1.60$ (s, 13H), 4.8 (m, 2H), 5.7 (m, 1H). – ^{13}C NMR (CDCl$_3$/TMS): $\delta = 24.64$ (d, $^{1}J_{C,H} = 135$ Hz), 26.10 + 30.78 (2 t, $^{1}J_{C,H} = 128$ Hz), 33.09 (s), 109.44 (t, $^{1}J_{C,H} = 154$ Hz), 148.35 (d, $^{1}J_{C,H} = 143$ Hz). – GC-MS (70 eV): $m/z = 136$ (73%, M$^+$), 79 (100, [C$_6$H$_7$]$^+$).

1-(1,2-Dibromoethyl)bicyclo[2.2.2]octane (**12**): The vinyl derivative **11** (1.5 g, 11 mmol) in 60 ml of dichloromethane was stirred with excess bromine for 10 h at room temperature. The solution was washed with aqueous NaHSO$_3$ and dried over sodium sulfate. After removal of the solvent the remainder was distilled at 150 °C/0.3 Torr to provide an almost colourless liquid (2.6 g, 80%) which was stored at −10 °C to the exclusion of light. – IR (film): 2940, 2915, 2855 (CH), 850, 780 cm^{-1} (CBr). – ^{1}H NMR (CDCl$_3$/TMS): $\delta = 1.60$ (s, 13H), 3.5 + 3.9 (m, 3H). – ^{13}C NMR (CDCl$_3$/TMS): $\delta = 23.80$ (d), 25.65 (t), 28.49 (t), 35.48 (t), 37.10 (s), 68.57 (d). – GC-MS (70 eV): $m/z = 217$ (19%), 215 (21, M$^+$ − Br), 135 (100, M$^+$ − HBr − Br).

$C_{10}H_{16}Br_2$ (296.1) Calcd. C 40.57 H 5.45 Found C 40.61 H 5.48

1-Ethynylbicyclo[2.2.2]octane (**1**): Dibromide **12** (0.80 g, 2.7 mmol) was solved in 45 ml of dry ethanol and stirred for 10 h at 100 °C with ca. 15 g of potassium hydroxide. The mixture was poured on ice water and saturated with sodium chloride. After extraction with diethyl ether and dichloromethane the organic layers were combined and dried over sodium sulfate. The solvents were removed by distillation over a short Vigreux column. The remaining liquid was solved in CCl$_4$ and again concentrated. The purity of the crude product (0.20 g, 47%) was sufficient enough for spectroscopic purposes. – IR (film): 3310 (≡CH), 2945, 2920, 2870, 2095 cm^{-1} (CH). – ^{1}H NMR (CCl$_4$/TMS): $\delta = 1.60$ (s, 13H), 1.86 (s, 1H). – ^{13}C NMR (CDCl$_3$/TMS): $\delta = 23.19$ (d, $^{1}J_{C,H} = 135$ Hz), 25.52 (t, $^{1}J_{C,H} = 131$ Hz), 26.20 (s), 31.88 (t, $^{1}J_{C,H} = 130$ Hz), 67.26 (d, $^{1}J_{C,H} = 247$ Hz), 92.14 (s/"d", $^{2}J_{C,H} = 46$ Hz). – GC-MS (70 eV): $m/z = 134$ (68%, M$^+$), 78 (100, M$^+$ − 2 C$_2$H$_4$).

In order to record the photoelectron spectrum a similar experiment was performed using perfluorohexane (Fluka) for extraction to avoid overlapping of product PE bands with those caused by traces of the solvent.

Recently Adcock[21] et al. published a series of ^{13}C-NMR studies of 4-substituted 1-cyano- and 1-ethynylbicyclo[2.2.2]octanes; the authors mentioned compound **1** having been synthesized by a different method as described above.

1,4-Bis(1,2-dibromoethyl)bicyclo[2.2.2]octane (**17**): To the diene **16** (0.80 g, 4.9 mmol) in 25 ml of CCl$_4$ excess bromine in CCl$_4$ was added. The reaction mixture was stirred for 8 h; an almost colourless precipitation (0.80 g, 34%) was separated by filtration; m.p. 170 °C. The filtrate was washed with diluted aqueous NaHSO$_3$ and dried over magnesium sulfate. Evaporation of the solvent provided a white solid (1.2 g, 53%), which was washed with ether and dried in vacuo, m.p. 130 °C. Both solid fractions showed identical spectra. – IR (KBr): 2940, 2915, 2860 (CH), 875, 635 cm^{-1} (CBr). – ^{1}H NMR (CDCl$_3$/TMS): $\delta = 1.28 + 1.63 + 1.79$ (q + s, 12H), 3.45 (m, 2H), 3.88 (m, 4H). – ^{13}C NMR (CDCl$_3$/TMS): $\delta = 28.61$ (t), 34.78 (t), 37.42 (s), 66.57 (d). – MS (70 eV): $m/z = 403$ (5%)/402 (2)/401 (14)/400 (2)/399 (15, M$^+$ − (H)Br), 108 (100, [C$_8$H$_{12}$]$^+$).

$C_{12}H_{18}Br_4$ (481.9) Calcd. C 29.91 H 3.76 Found C 30.04 H 3.75

1,4-Diethynylbicyclo[2.2.2]octane (**2**): Tetrabromide **17** (0.60 g, 1.2 mmol) was solved in 50 ml of anhydrous ethanol and 25 ml of dry dioxane; potassium hydroxide (ca. 10 g) was added. The mixture was stirred at 100 °C for 10 h and potassium bromide precipitated. The mixture was poured on ice water, saturated with sodium chloride, and extracted with diethyl ether and dichloromethane. The combined extracts were treated with neutral active charcoal and dried over sodium sulfate. Evaporation of the solvents provided nearly colourless crystals of **2** (0.20 g, 77%) being purified by sublimation at room temperature/0.01 Torr to afford colourless crystals (0.10 g, 52%), m.p. 162–164 °C. – IR (KBr): 3315 (≡CH), 2965, 2940, 2880 (CH), 2100 cm^{-1} (C≡C). – ^{1}H NMR (CDCl$_3$/TMS): $\delta = 1.73$ (s, 8H), 2.03 (s, 2H). – ^{13}C NMR (CDCl$_3$/TMS): $\delta = 26.03$ (s), 31.61 (t, $^{1}J_{C,H} = 153$ Hz), 68.05 (d, $^{1}J_{C,H} = 247$ Hz), 90.83 (s/"d", $^{2}J_{C,H} = 50$ Hz). – MS (70 eV): $m/z = 158$ (75%, M$^+$), 129 (100, M$^+$ − C$_2$H$_5$).

Preparation of the 1,4-Dihalobicyclo[2.2.2]octanes

Diethyl bicyclo[2.2.2]octane-1,4-dicarboxylate (**13**) was prepared according to Roberts[8] et al.: Succinyl succinate[22] was converted into the bicyclic derivative via alkylation with 1,2-dibromoethane in the presence of sodium hydride[23]. The two keto groups were removed by thioketalization and subsequent reduction with Raney nickel[8]. The diester **13** was converted into bicyclo[2.2.2]octane-1,4-dicarboxylic acid, the starting point for the synthesis of all dihalo derivatives.

1,4-Dichlorobicyclo[2.2.2]octane (**3**)[24] was prepared from bicyclo[2.2.2]octane-1,4-dicarboxylic acid according to Grob[25b] et al.: Lead tetraacetate (8.6 g, 19 mmol) was added in portions to the diacid (2.0 g, 10 mmol) and *N*-chlorosuccinimide (15.4 g, 115 mmol) in 25 ml of DMF and 5 ml of conc. acetic acid. The reaction mixture was stirred at 50 °C for 20 min. After cooling and extraction with pentane, dichloromethane, and diethyl ether the combined organic phases were washed with HClO$_4$ (20%), saturated aqueous potassium carbonate, and brine. After drying over sodium sulfate and removal of the solvents under reduced pressure a colourless solid (1.1 g, 60%) remained, which was purified by recrystallisation from *n*-hexane to provide colourless crystals (0.70 g, 36%), m.p. 228–231 °C (Ref.[24c] 234–235 °C). – IR (CHCl$_3$): 2950, 2920, 2870 (CH), 987, 828 cm^{-1} (CCl). – ^{1}H NMR (CDCl$_3$/TMS): $\delta = 2.22$ (s). – ^{13}C NMR (CDCl$_3$/TMS): $\delta = 37.84$ (t), 63.84 (s).

1,4-Dibromobicyclo[2.2.2]octane (**4**) was obtained by a modified *Cristol-Firth-Hunsdiecker* reaction[25]: Bicyclo[2.2.2]octane-1,4-dicarboxylic acid (2.0 g, 10 mmol) was heated to 70 °C together with red mercuric oxide (3.6 g, 16 mmol) and anhydrous magnesium sulfate (2.5 g, 21 mmol) in 75 ml of 1,2-dibromoethane; bromine (3.7 g, 23 mmol) was added, and the reaction mixture was kept at 70 °C for 14 h. After cooling and filtration the solution was dried over MgSO$_4$ and evaporated. The remaining solid (2.4 g, 88%) was purified by crystallization from acetone to provide colourless crystals (1.7 g, 60%), m.p. 253–256 °C (Ref.[25a] 248–249 °C, 44% yield; Ref.[25b] 252–253.5 °C, 40%). – IR (KBr): 2960, 2940, 2912, 2875, 2860 (CH), 960, 810 cm^{-1} (CBr). – ^{1}H NMR (CDCl$_3$/TMS): $\delta = 2.4$ (s). – ^{13}C NMR (CDCl$_3$/TMS): $\delta = 40.15$ (t, $^{1}J_{C,H} = 136$ Hz), 58.70 (s).

The bridgehead halogen exchange method developed by Pincock[26] did not succeed in converting **4** into the corresponding dichloro or diiodo derivatives!

Synthesis of the 1-Halobicyclo[2.2.2]octanes

Bicyclo[2.2.2]octane-1-carboxylic acid was synthesized according to Grob[27] et al.: Ethyl 2-(diethylamino)-3-cyclohexene-1-carboxylate[28] was converted into 1-(ethoxycarbonyl)-1,3-cyclohexadiene which reacted with maleic anhydride to give 1-(ethoxycarbonyl)bicyclo[2.2.2]oct-5-ene-2,3-dicarboxylic anhydride. Hydrogenation and reaction with potassium carbonate provided a saturated diacid, which was converted into ethyl bicyclo[2.2.2]octane-1-carboxylate (**8**) by treatment with lead tetraacetate in benzene and pyridine and subsequent hydrogenation; **8** was saponified to form the corresponding carboxylic acid, the precursor of the bridgehead halides.

1-Chlorobicyclo[2.2.2]octane (**5**) was synthesized in analogy to the 1,4-dichloro derivative **3**[24b]: Bicyclo[2.2.2]octane-1-carboxylic acid (1.2 g, 7.8 mmol) was stirred for 15 min at 60–65°C with *N*-chlorosuccinimide (6.0 g, 45 mmol) and lead tetraacetate (3.3 g, 7.5 mmol) in 10 ml of DMF and 2 ml of conc. acetic acid. After cooling the mixture was extracted with pentane, dichloromethane, and ether, the combined organic layers were washed with $HClO_4$ (20%), saturated aqueous potassium carbonate, and brine and were dried over sodium sulfate. After removal of the solvents under reduced pressure crude **5** (1.0 g, 89%) remained in form of a white solid, which was sublimed twice and then completely purified by preparative VPC (20% carbowax 20M on chromosorb R NAW, 60/80 mesh, 4m; oven temp.: 120°C). M.p. 101–103°C (Ref.[24b] 103–104°C, 95% yield). – IR ($CHCl_3$): 2945, 2918, 2865 (CH), 900, 840 cm^{-1} (CCl). – ^1H NMR ($CDCl_3$/TMS): $\delta = 1.45-2.2$ (br m).

1-Bromobicyclo[2.2.2]octane (**6**): Bicyclo[2.2.2]octane-1-carboxylic acid was converted into the bromo derivative **6** by means of a modified *Cristol-Firth-Hunsdiecker* reaction[29]: The acid (1.2 g, 7.8 mmol) and red mercuric oxide (2.0 g, 9.2 mmol) in 30 ml of dibromomethane were heated to 75°C; bromine (1.3 g, 8.1 mmol) in 5 ml of dibromomethane was added, and the mixture was stirred for 9 h at that temperature. After cooling and filtration the solution was washed with aqueous $NaHSO_3$ and brine. After drying over sodium sulfate and evaporation of the solvent the remainder was sublimed at 70°C/0.9 Torr to provide colourless crystals (0.70 g, 46%) of **6**, m.p. 65°C (ref.[27] 66–68°C). – IR ($CHCl_3$): 2950, 2920, 2865 (CH), 629 cm^{-1} (CBr). – ^1H NMR ($CDCl_3$/TMS): $\delta = 1.6-2.3$ (br m).

CAS Registry Numbers

1: 96454-73-8 / **2**: 105858-44-4 / **3**: 1123-39-3 / **4**: 10364-04-2 / **5**: 2064-03-1 / **6**: 7697-09-8 / **8**: 31818-12-9 / **8** (free acid): 699-55-8 / **8** (5-ene-2,3-dicarboxylic anhydride): 105881-97-8 / **9**: 2574-42-7 / **10**: 2064-65-3 / **11**: 96454-91-0 / **12**: 105858-43-3 / **13**: 1659-75-2 / **13** (free acid): 711-02-4 / **14**: 826-45-9 / **15**: 84774-84-5 / **16**: 88393-19-5 / (*R**,*R**)-**17**: 105881-96-7 / (*R**,*S**)-**17**: 105881-98-9 / $Ph_3P^+Me \cdot I^-$: 2065-66-9 / 1-(ethoxycarbonyl)-1,3-cyclohexadiene: 3725-40-4

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