

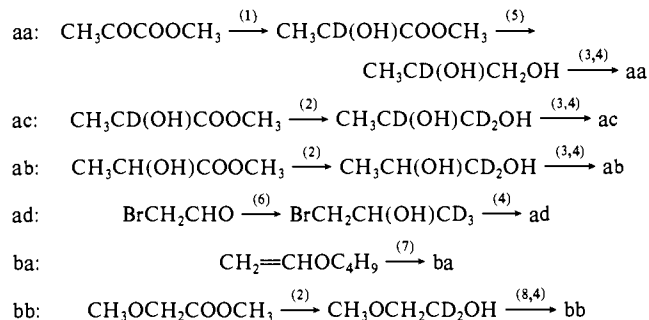
tight activated complex. Alternatively, it is conceivable that the 1,2-H isomerization $a \rightarrow e(\bar{A})$ at these higher energies produces $\text{CH}_3\text{COCH}_3^+$ with sufficient excess vibrational energy in the newly formed methyl to result in its favored loss in a non-ergodic process. This mechanism is demonstrated in the preceding paper¹¹ for excited $\text{CH}_3\text{COCH}_3^+$ ions formed by 1,3-H isomerization from $\text{CH}_3\text{C}(\text{OH})\text{CH}_2^+$.

Experimental Section

The tandem mass spectrometer²⁵ and experimental conditions are described in the preceding article.¹¹ Propene oxide was obtained from Aldrich and ad from Merck, and methyl vinyl ether was prepared according to ref 26. Synthetic conditions for the labeled compounds were the following: (1) NaBD_4 , methanol; (2) LiAlD_4 , ether; (3) HBr (gas); (4) KOH ; (5) LiAlH_4 , ether; (6) CD_3MgI , ether; (7) CD_3OH , $\text{Hg}(\text{OC}_2\text{H}_5)_2$; (8) PBr_3 , pentane.

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He I and He II Photoelectron Spectra and CNDO/S and MNDO MO Calculations of Some Bridged [10]Annulenes

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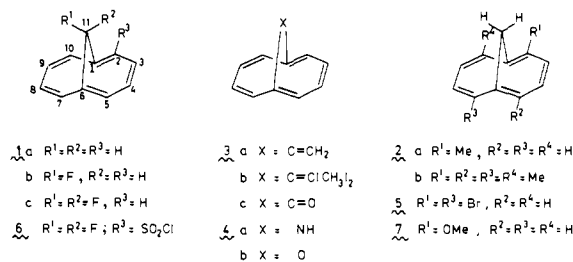
Abstract: He I and He II PE spectra of a series of 13 bridged [10]annulenes are reported. For all compounds the order of the observed π MO's of the peripheral ring from high to low energy is $7a_2$, $13a_1$, $9b_1$, and $9b_2$ (based on C_{2v} symmetry). For 1,6-methano[10]annulene (**1a**) and 11,11-difluoro-1,6-methano[10]annulene (**1c**), the ionization energies of the π MO's have been calculated by CNDO/S and MNDO calculations. With **1b**, **1c**, **2a**, **2b**, **3a**, and **3b** the observed perturbation on the π system as a result of the introduction of substituents on the bridge and in the peripheral ring appears to be distributed roughly to the same degree over the π MO's. Calculations for **2a** in which the methyl substituent is taken as a first-order perturbation on the perimeter π MO's leads to essentially the same conclusion. Computer plots of the upper four π MO's of **1a**, constructed from the eigenvectors calculated by CNDO/S and MNDO, show that the ring π system is locally not orthogonal to the σ framework. The observed relatively large stabilization of the $9b_2$ as compared to the other π MO's of **3a** and **3b** may be explained by a *through-space* interaction of this MO with the carbon p_x orbital of the bridge.

1,6-Methano[10]annulene (**1a**), synthesized elegantly by Vogel,¹ is classified to be a Hückel aromatic hydrocarbon.² It formally results upon replacing in [10]annulene the hydrogens at C¹ and C⁶ by a methylene group.

The nonplanar perimeter of **1a**³ and its derivatives shows a high reactivity⁴⁻⁶ and a very high positional selectivity toward electrophilic substitution.⁴⁻⁸ Sulfonation with the dioxan-SO₃ complex,⁴ bromination with Br₂ and with *N*-bromosuccinimide,⁶⁻⁸ and isocyanosulfonylation⁷ all yield exclusively the 2-substituted product. Also sulfonation of, e.g., 11-methylene- (**3a**),⁵ 11-oxido- (**4b**),⁹ and 11,11-difluoro-1,6-methano[10]annulene (**1c**)⁹ with 1 equiv of dioxane-SO₃ yields exclusively the 2-sulfonic acid.

To obtain a better insight into the electronic structure of the bridged [10]annulenes, we have made a UV photoelectron spectroscopy (PES) study of **1-7** and have performed CNDO/S and MNDO MO calculations on **1a** and **1c**.

A decade ago Boschi, Schmidt, and Gfeller observed that in the He I spectrum of **1a**¹⁰ the degeneracy of the $1e_{1g}$ and $1e_{2u}$ π



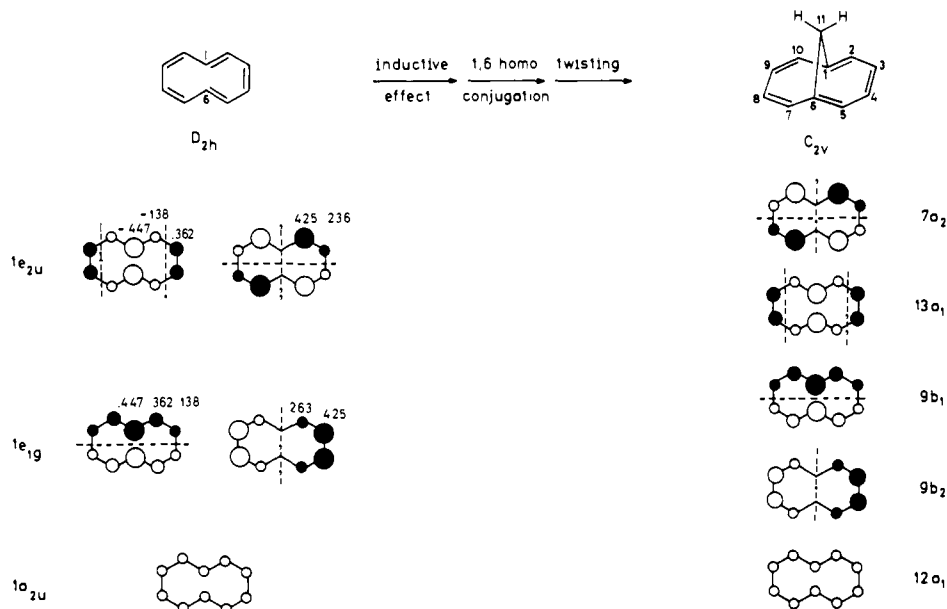
MO levels of the [10]annulene with D_{2h} symmetry is removed. This lifting of the degeneracy may a priori be explained in terms

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- (4) Lammertsma, K.; Cerfontain, H. *J. Am. Chem. Soc.* **1978**, *100*, 8244.
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Chart I. Splitting of the π MO's of the [10]Annulene with D_{2h} Symmetry and 1,6-Methano[10]annulene (**1a**) with C_{2v} SymmetryTable I. Experimentally Determined Ionization Energies (I_J) of MO's of the Studied [10]Annulenes^a

entry	MO	substrate												
		1a	1b	1c	2a	2b	3a	3b	3c	4a	4b	5	6	7
1	7a ₂	7.92	8.10	8.19	7.71	7.22	7.98	7.90	8.47	8.01	8.14	8.09	8.90	7.56
2	13a ₁	8.39	8.67	8.79	8.19	7.85	8.23	8.20	9.14	8.01	8.45	8.73	9.27	8.23
3	9b ₁	9.25	9.51	8.73	9.00	8.47	9.29	9.14	10.36	9.59	10.10	9.15	10.26	8.90
4	9b ₂	10.36	10.62	10.70	10.17	9.68	10.47	10.32	10.80	10.64	10.74	10.66 ^b		10.10
5	12a ₁					10.52								
6	$\pi_{C=C}$						9.46	8.48						
7	O lone pair								8.76		10.25			
8	N lone pair									9.84				
9	Br p lone pair											10.66 ^b		
10	Br σ lone pair											10.66 ^b		

^a The ionization energies are in -eV, ± 0.03 . ^b The fourth ionization band in the PE spectrum of **5** is assigned to the 9b₂ and the σ and p lone pairs of bromine (see text).

of three types of interactions (Chart I), viz. (i) the strong homoconjugative transannular interaction¹⁰⁻¹³ between the 2p AO's of C¹ and C⁶, (ii) the inductive destabilization^{10-12,14} by the bridging methylene group, and (iii) the destabilization due to the twisting of the bonds in the peripheral ring.^{10,11,15} According to Boschi, the nondegeneracy of the π MO levels of **1a** could be accounted for satisfactorily by considering the first two types of interaction, and accordingly the π MO order depicted in Chart I was proposed.¹⁰ This approach completely ignores the third (destabilizing) effect $\Delta I_J^{\text{twist}}$, given by eq 1, where $\theta_{a,b}$ are the C^a-C^b bond twist

$$\Delta I_J^{\text{twist}} = [2 \sum_{a,b} C_{Ja} C_{Jb} (\cos \theta_{a,b} - 1)] \beta^0 \quad (1)$$

angles ($\theta_{1,2} = 34^\circ$, $\theta_{2,3} = 19.7^\circ$, $\theta_{3,4} = 0^\circ$)³ and β^0 is the resonance integral of an undistorted π bond in [10]annulene calibrated by a least-squares treatment to a value of -2.734 eV.^{12,16} This leads

to a $\Delta I_J^{\text{twist}}$ for the 7a₂, 13a₁, 9b₁, and 9b₂ MO's of 0.14, 0.17, 0.70, and 0.14 eV, respectively. However, these values, especially that of 9b₁, are not reflected in the PE spectrum of 1,6-methano[10]annulene.

Batich, Heilbronner, and Vogel suggested that for bridged [10]- and [14]annulenes eq 1 is probably not applicable.¹² They proposed that the "true" angle $\theta_{a,b}$ between the AO's of a given pair of adjacent annulene carbons *a* and *b* is smaller than the twist angle $\theta_{a,b}$, as determined by X-ray analysis. This infers that "the resulting π -ribbon stretches elastically around the periphery and will not necessarily be locally perpendicular to the σ -bonds".¹² Mock, Radom, and Pople made a similar proposition as to the π bonds of deformed ethylenes.^{17,18} Recently, it was proposed on the basis of STO-3G calculations on bent and twisted ethylene that the relative insensitivity of the π -electron orbital energy toward these nonplanar distortions may also be attributed to the small sizes of the individual contributions associated with each of the three internal coordinates and to the compensation of such effects and/or the cross terms between pairs of internal coordinates.¹⁹

In the last decade various types of MO calculations on **1a** were reported, viz. HMO,^{10,12} EHT,²⁰ CNDO,²¹ CNDO/2,²² INDO,²²

- (9) Lambrechts, H. J. A.; Cerfontain, H., unpublished data.
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 (12) Batich, C.; Heilbronner, E.; Vogel, E. *Helv. Chim. Acta* **1974**, *57*, 2288.
 (13) Dewey, H. J.; Deger, H.; Frölich, W.; Dick, B.; Klingensmith, K. A.; Hohlneicher, G.; Vogel, E.; Michl, J. *J. Am. Chem. Soc.* **1980**, *102*, 6412 and references cited therein.
 (14) No evidence was found for a hyperconjugative interaction and accordingly this type of interaction was proposed to be at most very small.^{10,13,15}
 (15) Kolc, J.; Michl, J.; Vogel, E. *J. Am. Chem. Soc.* **1976**, *98*, 3935.
 (16) Broglie, F.; Heilbronner, E. *Theor. Chim. Acta* **1972**, *26*, 289.

- (17) Mock, W. L. *Tetrahedron Lett.* **1972**, 475.
 (18) Radom, L.; Pople, J. A.; Mock, W. L. *Tetrahedron Lett.* **1972**, 479.
 (19) Honegger, E.; Schmelzer, A.; Heilbronner, E. *J. Electron Spectrosc. Relat. Phenom.* **1982**, *28*, 79.
 (20) Gravezotti, A.; Simonetta, M. *Helv. Chim. Acta* **1976**, *59*, 2984.
 (21) Klenk, H.; Stohrer, W.-D.; Effenberger, F. *Chem. Ber.* **1976**, *109*, 777.

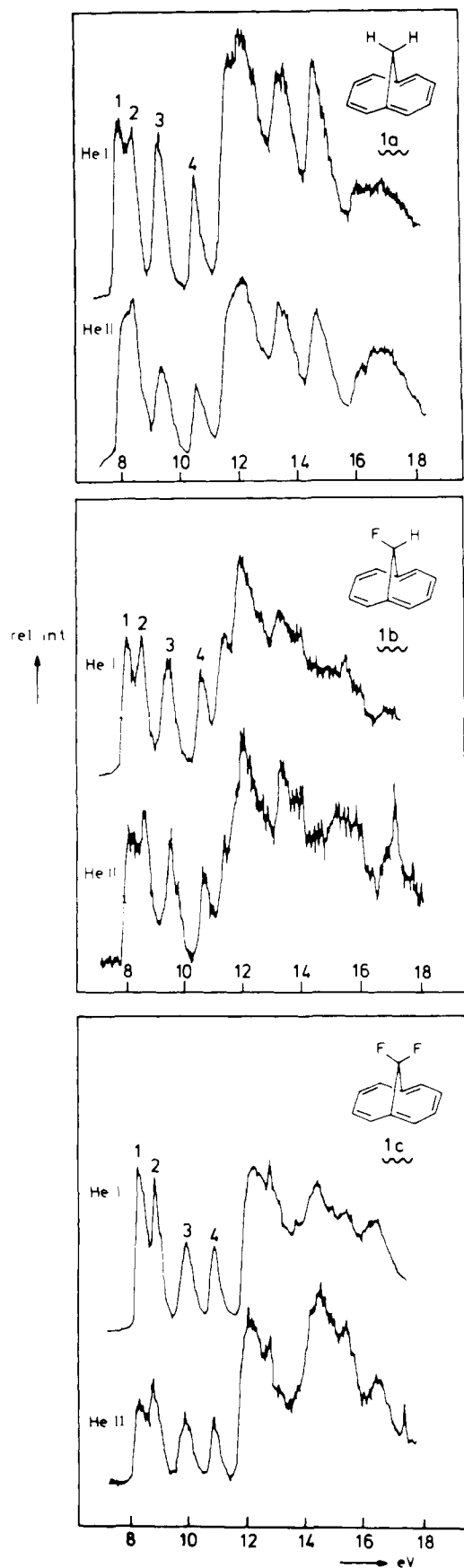


Figure 1. He I and He II photoelectron spectra of 1,6-methano[10]annulene (**1a**), 11-fluoro-1,6-methano[10]annulene (**1b**), and 11,11-difluoro-1,6-methano[10]annulene (**1c**).

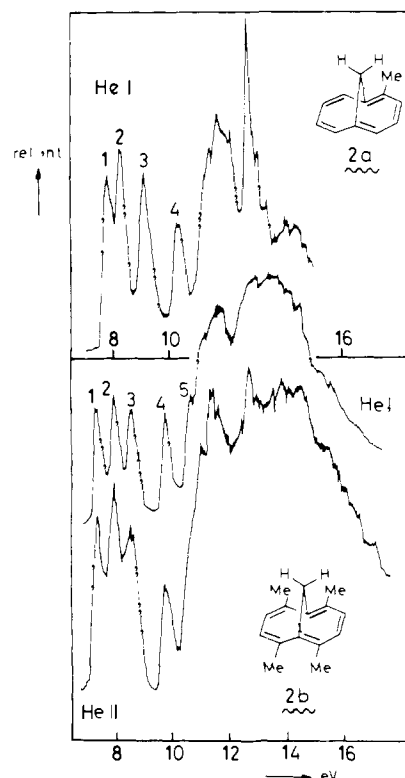


Figure 2. He I and He II photoelectron spectra of 2-methyl- (**2a**) and 2,5,7,10-tetramethyl-1,6-methano[10]annulene (**2b**).

and ab initio calculations (fragment method,²² STO-2G,²³ STO-3G,²³ and 4-31G basis sets²³).

Results

Assignment of the Photoelectron Spectra. He I and He II PE spectra of the substrates 1–7 have been measured. The spectra are shown in Figures 1–5. The measured π -orbital ionization energies (I_j 's) of 1–7 are collected in Table I. The interpretation of the data of Table I was made on the basis of Koopmans' theorem.²⁴

In all the PE spectra four bands are present in the region -7.0 to -10.5 eV which correspond to the highest four occupied π MO's of the annulene ring. The $12a_1$ π MO is at lower energy and hidden under the broad σ bands, except with **2b**, where it is seen at -10.52 eV.

The assignment of the π MO's to the observed ionization bands was made on the basis of (i) the variations in the band positions due to substitution on the annulenes, (ii) the variations in the relative band intensities on going from He I to He II as ionizing source,²⁵ and (iii) a comparison of the observed with the calculated ionization energies (see later).

Molecular Orbital Calculations. CNDO/S²⁷ and MNDO²⁸ MO calculations have been made for **1a** and **1c** using for their geometry

(22) Grunewald, G. L.; Uwaydah, I. M.; Christoffersen, R. E.; Sprangler, D. *Tetrahedron Lett.* **1975**, 933.

(23) Farnell, L.; Radom, L. *J. Am. Chem. Soc.* **1982**, *104*, 7650.

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

(25) Band intensities are theoretically best described as photoionization cross sections which mainly depend on the photon energy and the electron density distribution in the initial orbital.²⁶ A change in the energy of an incoming photon results in a change of the photoionization cross section and consequently in a change in intensity of the observed ionization bands which will be different for different types of electrons. Thus the use of both He I and He II photons as the ionization source is a powerful tool for the assignment of different types of ionization. An excellent treatment on the subject is given in ref 26.

(26) Schweig, A.; Thiel, W. *J. Chem. Phys.* **1974**, *60*, 951.

(27) (a) Del Bene, J.; Jaffè, H. H. *J. Chem. Phys.* **1968**, *48*, 1807. (b) Bigelow, R. W. *Ibid.* **1977**, *66*, 4241. (c) K. Nishimoto, K.; Mataga, N. *Z. Phys. Chem. (Frankfurt am Main)*, **1957**, *12*, 335.

(28) Dewar, M. J. S.; Thiel, W. *J. Am. Chem. Soc.* **1977**, *99*, 4633.

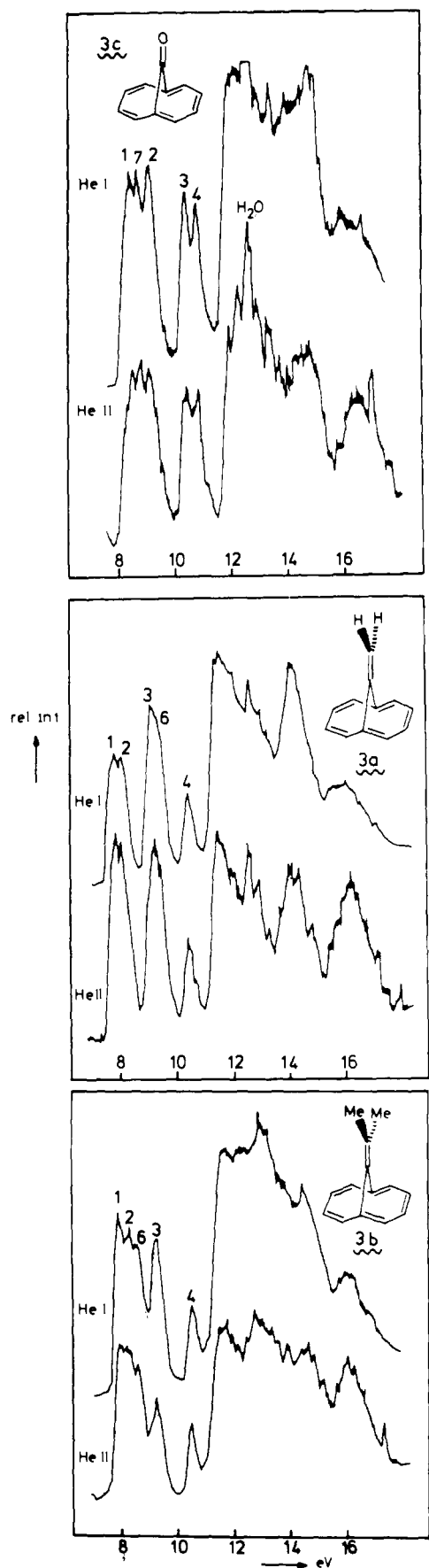


Figure 3. He I and He II photoelectron spectra of 11-methylene- (3a), 12,12-dimethyl-11-methylene- (3b), and 11-oxo-1,6-methano[10]annulene (3c).

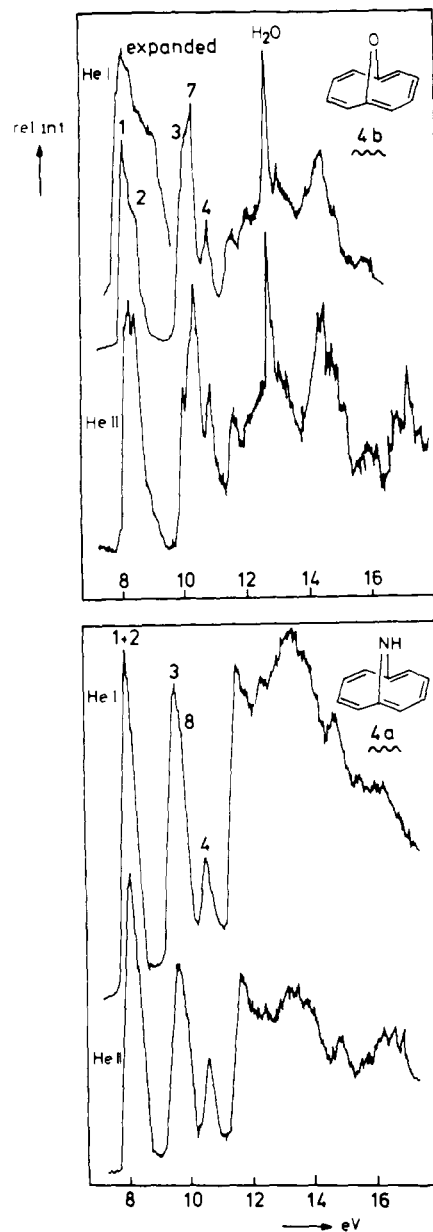


Figure 4. He I and He II photoelectron spectra of 11-imino- (4a) and 11-oxido-1,6-methano[10]annulene (4b).

Table II. Observed and Calculated Perturbation on the Upper Four π MO's of 1a as a Result of Methyl Substitution at C²

MO	Δ/J , eV		
	exptl	CNDO/S	MNDO
7a ₂	0.21	0.19	0.19
13a ₁	0.20	0.12	0.13
9b ₁	0.25	0.14	0.18
9b ₂	0.19	0.14	0.12

the reported^{3,29} crystallographic data. The MO eigenvalues thus obtained are tabulated in Figure 6. The CNDO/S calculation yields the π -MO orbital order as proposed by Boschi, Schmidt, and Gfeller.¹⁰ With MNDO the 7a₂ and 13a₁ MO's are calculated to be degenerate.

The MNDO calculated 7a₂, 13a₁, 9b₁, and 9b₂ π MO's of 1a are visualized as PICTOR³⁰ plots in Figure 7. The perturbation

(29) Pilati, T.; Simonetta, M. *Acta Crystallogr., Sect B* 1976, B32, 1912.

(30) The program PICTOR was written by J. N. Louwen in Fortran-77. It visualizes the participation of the σ and π orbitals in the MO's in a fully descriptive (i.e., not approximate) manner: in principle the PICTOR plots can be reconverted again into the original eigenvectors.

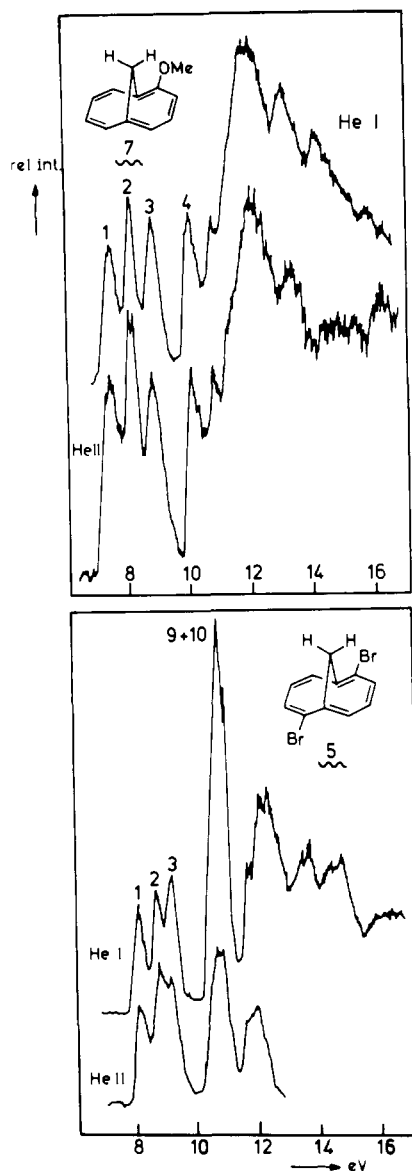


Figure 5. He I and He II photoelectron spectra of 2,5-dibromo- (5) and 2-methoxy-1,6-methano[10]annulene (7).

on the energies of the π MO's, ΔI_J , of **1a** as a result of the introduction of a methyl group at C² has been calculated from the canonical orbitals of **1a** obtained by both CNDO/S and MNDO with use of eq 2³¹ in which C_μ is the coefficient of ψ (the

$$\Delta I_J = [C_\mu^2 + 1/3(C_\nu^2 + C_\xi^2)]\delta\alpha \quad (2)$$

molecular orbital corresponding to the ionization band) on atom μ (the site of substitution), C_ν and C_ξ are the respective coefficients on the neighboring atoms ν and ξ , and $\delta\alpha$ is an adjustable substituent parameter (which is 1.0 eV for Me³¹). The results are summarized in Table II.

Discussion

The CNDO/S and MNDO MO calculations of **1a** agree with the assignment made previously¹⁰ on the basis of simple Hückel MO arguments and with the results of an ab initio (fragment method) calculation.²² Recently, advanced ab initio MO calculations on **1a** were performed with use of STO-2G, STO-3G, and 4-31G basis sets.²³ With the first basis set the bisnorcaradienic form of **1a** was calculated to be the more stable one and with the latter two the annulenic form, thus illustrating the relatively small energy difference of the two forms.

(31) Heilbronner, E.; Hornung, V.; Pinkerton, F. H.; Thames, S. F. *Helv. Chim. Acta* **1972**, *55*, 289.

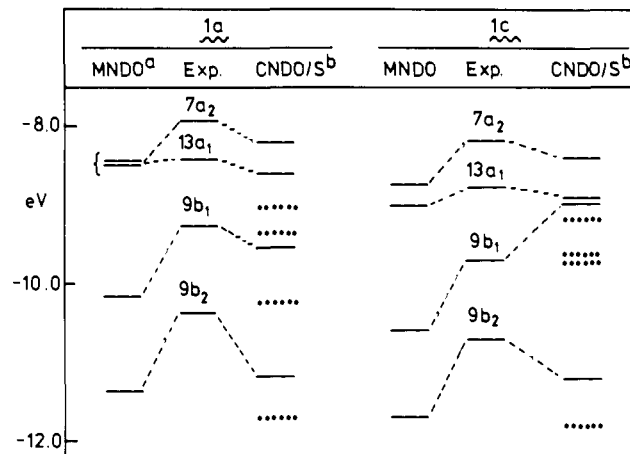


Figure 6. Correlation diagram of CNDO/S, MNDO, and experimentally determined energies of the $7a_2$, $13a_1$, $9b_1$, and $9b_2$ MO's of **1a** and **1c**. (a) The dotted lines refer to the calculated data from which the solid lines were obtained by application of the Bigelow correction $I_J^{corr} = 11.364 \ln (I_J^{calcd}/4400)$.^{26b} (b) The $7a_2$ and $13a_1$ MO are calculated to be degenerate.

On going from the He I to the He II PE spectrum of **1a** there is a relative decrease in the intensity of the $7a_2$ band at -7.92 eV, the $9b_1$ band at -9.25 eV, the $9b_2$ band at -10.36 eV and a relative increase in the $13a_1$ band intensity at -8.39 eV.³² This facilitated the assignment of the $7a_2$ and $13a_1$ π MO's in **1b**, **1c**, **2b**, **3b**, **4b**, and **5**.

From the PE spectra of **1a-c** it follows that the replacement of the bridge hydrogens by fluorine leads to a stabilization of the four π MO's. ΔI_J ³³ for $7a_2$, $13a_1$, $9b_1$, and $9b_2$ is -0.18 , -0.28 , -0.26 , and -0.26 eV for **1b** and -0.27 , -0.40 , -0.48 , and -0.34 eV for **1c**. On the basis of the orbital character (cf. Figure 7) of the four highest π MO's, the inductive effect of fluorine is expected to affect the $13a_1$ and $9b_1$ much more than the $7a_2$ and $9b_2$. Although this trend is apparent with **1c**, the difference in the stabilization of the π MO's is less than, e.g., going from toluene³⁴ to benzyl fluoride,³⁵ where the π_{b1} and π_{a2} are stabilized by -0.83 and -0.56 eV, respectively. With **1b** and **1c**, the perturbation as a result of the introduction of fluorine at C¹¹ appears to be distributed roughly to the same degree over all four π MO's, in agreement with the results obtained from the MNDO MO calculation (Figure 6). The same phenomenon was observed upon introducing two fluorines in norbornadiene.³⁶

The PICTOR plots of the $7a_2$, $13a_1$, $9b_1$, and $9b_2$ π MO's of **1a** (Figure 7) show that the σ and π orbitals in the ring are locally not orthogonal. This conclusion is in agreement with an earlier suggestion.¹² This σ - π non-orthogonality was recently applied to explain that the bromo addition on reaction of **1a** with Br_2 at -60 °C in CHCl_3 occurs at positions 2 and 5, both *syn* to the CH_2 bridge.^{37,38}

Upon introducing in **1a** a methyl at C², all four π MO's are destabilized to the same extent within experimental error (for $7a_2$, $13a_1$, $9b_1$, and $9b_2$, $\Delta I_J = 0.21$, 0.20 , 0.25 , and 0.19 eV, respectively). This is in sharp contrast to the observations in the benzene and naphthalene series, since the ΔI_J 's for the π_{b1} and π_{a2} π MO's on going from benzene³⁴ to toluene³⁴ are 0.52 and 0.00 eV, respectively, and the ΔI_J 's for the upper three π MO's on going from naphthalene³⁹ to 1-methylnaphthalene³¹ are 0.20 , 0.14 , and 0.40

(32) The decrease in intensity of the $7a_2$ π MO cannot be explained in terms of a hyperconjugative interaction between the σ orbitals of the $-\text{CH}_2-$ bridge and the p orbitals on C², C⁵, C⁷, and C¹⁰ since the $7a_2$ π MO has two nodal planes through the bridge (Chart I). It is most likely due to a difference in the two-center term $[C_\nu C_\mu^* M_\nu M_\mu^* I_{\nu\mu}]$.

(33) A negative value of ΔI_J (eV) infers relative stabilization of this orbital.

(34) Debies, T. B.; Rabalais, J. W. *J. Electron Spectrosc. Relat. Phenom.* **1972**, *1*, 355.

(35) Schmidt, H.; Schweig, A. *Tetrahedron Lett.* **1973**, 981.

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(38) Scholl, T.; Lex, J.; Vogel, E. *Angew. Chem.* **1982**, *94*, 924.

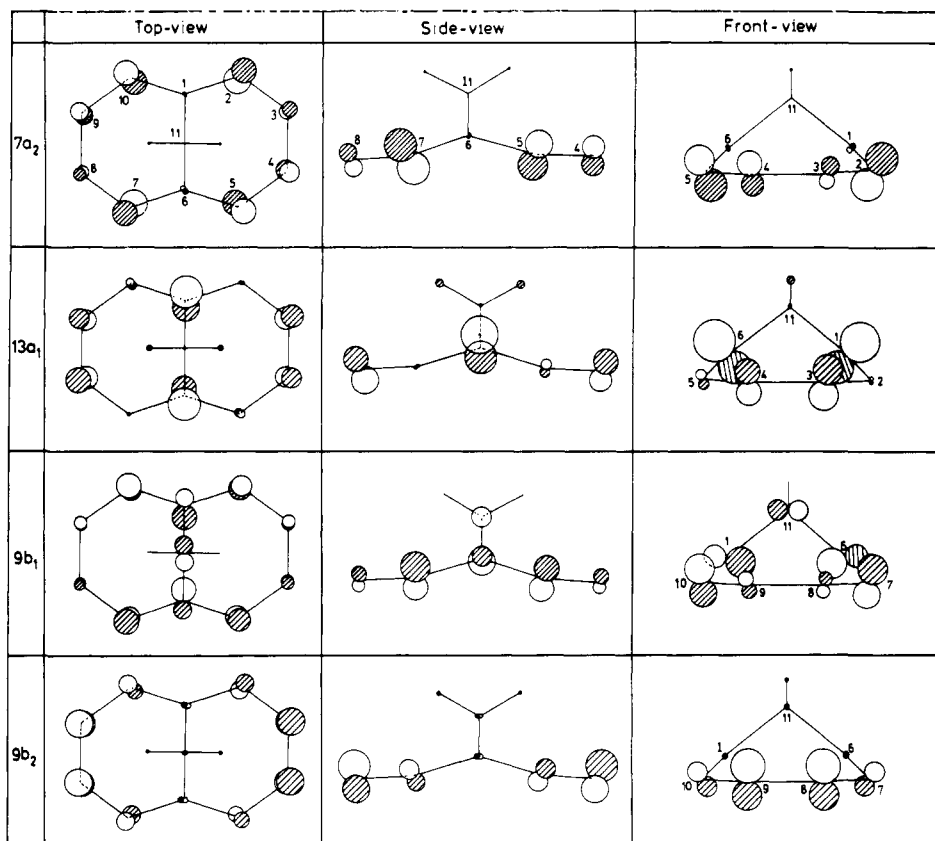


Figure 7. PICTOR plots of the $7a_2$, $13a_1$, $9b_1$, and $9b_2$ π MO of **1a**.

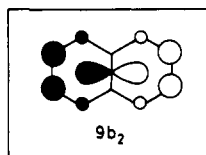


Figure 8. Through-space interaction of the $9b_2$ π MO with the bridge carbon p_x orbital in **3a**, **3b**, and **3c**.

eV, respectively. A first-order perturbation calculation from the canonical orbitals of **1a** calculated by both CNDO/S and MNDO with use of eq 2 leads to the same result (Table II). In **2b**, where all four α hydrogens are replaced by a methyl, a comparable destabilization of all four bands is observed, which is in fact *circa* 4 times the destabilization upon replacing one α hydrogen in **1a** by a methyl as observed for **2a** (cf. Table II).

The PE spectra of **3a**, **3b**, and **3c** exhibit additional bands to those in the PE spectrum of **1a**, viz. at -9.46 , -8.48 , and -9.14 eV, respectively, due to the ejection of a π electron from the bridge moieties. The observed destabilization of the $\pi_{C=C}$ ionization band of **3b** relative to that of **3a** by 0.98 eV is of the same order as that on going from ethylene to 1,1-dimethylethylene (1.07 eV).^{31,40,41} The significant destabilization (0.16 eV) of the $13a_1$ π MO of **3a** is explained by a level interaction between a σ orbital of relatively high energy of the $C=CH_2$ moiety and the $13a_1$ π MO of the peripheral ring which is the only π orbital with the correct symmetry (Chart I). From a comparison of the PE spectra of **3a** and **1a** it follows that the $9b_2$ π MO of **3a** is significantly stabilized by the ethylene bridge (-0.11 eV). This may be explained in terms of a *through-space* interaction between the p_x orbital of the bridge C^{11} atom with the ring π system (Figure 8).⁴² When the two

hydrogens of the ethylene bridge in **3a** are both replaced by methyl, the $7a_2$, $13a_1$, $9b_1$, and $9b_2$ π MO's are destabilized by 0.08 , 0.03 , 0.15 , and 0.15 eV, respectively. This can only be explained in terms of a *through-bond* interaction between the ethylene and the ring π system. The ΔI_1 order observed, viz. $9b_2 = 9b_1 > 7a_2 > 13a_1$, then infers that this interaction decreases in that order. The difference in energy of the $9b_2$ π MO's of **3b** and **1a** of 0.04 eV is the net result of the two types of interaction, viz. the stabilizing *through-space* interaction of the bridge p_x orbital with the ring π system (-0.11 eV, see **3a**) and the destabilizing inductive effect exerted by the two methyls on the ethylene bridge (0.15 eV). The ionization band due to the ejection of an electron from the oxygen lone pair of the carbonyl bridge oxygen atom of **3c** is destabilized by 0.95 and 0.19 eV compared to that of acetone⁴⁵ and diisopropyl ketone,⁴⁵ respectively. The four π -ionization bands of the ring of **3c** are all stabilized compared with those of **1a** due to the electron-withdrawing effect of the carbonyl bridge⁴² and the longer distance between C^1 and C^6 (2.348 Å in **3c**⁴⁶ vs. 2.235 Å in **1a**³). The stabilization order is $9b_1 > 13a_1 > 7a_2 > 9b_2$ (-1.11 , -0.75 , -0.55 , and -0.44 eV, respectively). The stabilization effect is more operative in the $9b_1$ than in the $13a_1$ π MO, since from the MO calculations on **1a** it appears that there is a significant participation

(42) The UV spectra of **1a**, **3a**, **3b**, and **3c** are superimposable and it was concluded⁴³ that there would be no interaction between the two π systems of **3c**. However, this conclusion is based on the absorption of the annulene system only and is therefore somewhat premature. Recently, we found that the fluorescence intensity of the peripheral ring of **3c** is $\approx 50\%$ of that of **1a** [$\lambda_{max}^f(CH_3CN) = 429$ nm and $\lambda_{exc} = 390$ nm] and that there is no long-wavelength fluorescence band.⁴⁴ The electron-withdrawing carbonyl group apparently quenches the fluorescence of the electron-donating perimeter. Since the two π systems are close to orthogonal, the quenching is thought to proceed mainly *through-bond*. It should be recalled, however, that the PE spectra of **3a** and **3b** clearly demonstrate *through-space* interaction between the two π systems.

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of the p orbital on C¹¹ in the 9b₁ π MO (cf. Figure 7), and since the p orbitals on C¹ and C⁶ have the opposite sign in the 9b₁ and the same sign in the 13a₁.

The He I spectrum of **4a** consists of three bands in the region -8.0 to -11.0 eV. The first band at -8.01 eV is assigned to ionizations of the 7a₂ and 13a₁ π MO. The second band is assigned to the ejection of an electron of the 9b₁ π MO and the nitrogen lone pair at -9.59 and -9.84 eV, respectively. The band at -10.64 eV is assigned to ionization of the 9b₂ π MO. The ionization energy of the nitrogen lone pair at -9.84 eV compares well with that reported for ethylenimine (-9.8 eV).⁴⁷ The 7a₂, 9b₁, and 9b₂ π MO's of **4a** are all stabilized compared to those of **1a**, the ΔI_j's being -0.09, -0.34, and -0.28 eV, respectively. For the 7a₂ and 9b₂ π MO this may be explained by the inductive electron-withdrawing effect of the bridge nitrogen and for the 9b₁ by the same two effects as discussed for the 9b₁ π MO of **3c** (see before). The destabilization of the 13a₁ π MO is the result of two opposing interactions, viz. a stabilization as a result of the inductive electron-withdrawing effect of nitrogen and a destabilization most probably due to a level interaction of the ring π system with the σ levels of the bridge (see before).

In the PE spectrum of **4b** the band due to ionization of an electron from the lone pair of oxygen is not immediately apparent. Usually these types of ionizations are sharp and of somewhat greater intensity than those of π MO's especially in the He II spectra, as a result of the difference in cross section of the O_{2p} and C_{2p} electrons with the He I and He II photons.⁴⁸ The spectrum of **4b** is different from that of **3c** in that the oxygen lone pair is now in between the 9b₁ and 9b₂ band. The ionization energy of the oxygen lone pair (-10.25 eV) is in good agreement with that reported for ethylene oxide (-10.57 eV).⁴⁷ The π MO's are all stabilized compared to those of **1a**, the ΔI_j's for the 7a₂, 13a₁, 9b₁, and 9b₂ being -0.22, -0.06, -0.85, and -0.38 eV, respectively. The stabilization of these MO's may be explained in a similar fashion as for the π MO's of **4a** (see before). The larger stabilization of the 7a₂ and 9b₂ π MO of **4b** compared with **4a** is explained by the larger inductive electron-withdrawing effect of oxygen compared to nitrogen. With the 13a₁ π MO of **4b** the inductive effect is dominating.

The larger stabilization of the 9b₁ π MO of **4b** (-0.85 eV) compared to **4a** (-0.34 eV) may be explained in terms of the difference in the electron affinity of the participating 2p orbital of the bridging heteroatom, which is ca. -11 and ca. -8 eV for oxygen and nitrogen, respectively.⁴⁸

The He I spectrum of **5** consists of four bands in the region -8.0 to -11.5 eV. The relative intensity of the second band increases while those of the first and the fourth bands decrease upon using the He II photons, and the decrease is greater for the

fourth than the first band. The fourth band is assigned to ionizations of the 9b₂ π MO and the σ and p lone pairs of the bromines together. As a result of the very low cross section of the Br_{3p} orbitals with the He II photons,⁴⁹ the ionization from the 9b₂ π MO can unambiguously be assigned to be within the complex band at -10.66 eV. The difference in energy of the 7a₂, 13a₁, and 9b₁ π MO between **5** and **1a** are -0.17, -0.34, and 0.10 eV, respectively. They result from two opposing effects, viz. a stabilizing inductive electron withdrawing and a destabilizing conjugative effect of the bromines. With the 7a₂ and 13a₁ the first effect is dominating, whereas with the 9b₁ the latter dominates.

The 7a₂, 13a₁, and 9b₁ π MO's of **6** are significantly stabilized compared to those of **1c**, viz. by -0.71, -0.48, and -0.53 eV, respectively. This is attributed to the (inductive) electron-withdrawing effect of the -SO₂Cl group. The higher stabilization of the 7a₂ as compared with the other two MO's is in line with the expectations on the basis of the orbital character (Figure 7).

From a comparison of the UP spectra of **7** and **1a** it follows that the introduction of **1a** of a methoxy group at C² affects all the π MO's, the ΔI_j for the 7a₂, 13a₁, 9b₁, and 9b₂ being 0.36, 0.16, 0.35, and 0.26 eV, respectively. A comparable trend is observed in the naphthalene series, where the ΔI_j's for the upper three π MO's on going from naphthalene to 1-methoxynaphthalene are 0.43, 0.11, and 0.53 eV.⁵⁰ The destabilization is mainly the result of two types of interaction, viz. (i) a level interaction⁵¹ between the p lone pair of the oxygen atom and the ring π MO's which leads to destabilization at least for the upper four ring π MO's (I_j^{CH₃OH} = -10.94 eV) and (ii) the stabilizing inductive electron-withdrawing effect of the methoxy substituent.

Experimental Section

The annulenes **1a**,¹ **2a**,²¹ and **6**⁵² have been synthesized according to known procedures, and the others were generously supplied as gifts by Prof. E. Vogel, University of Cologne, BRD. The PE spectra have been recorded on a Perkin-Elmer PS 18 photoelectron spectrometer modified with a Helectros He I/He II hollow cathode light source. The spectra were calibrated with respect to Ar, Xe, and He as internal calibrants. No correction was made for the analyzer dependence.

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Registry No. **1a**, 2443-46-1; **1b**, 71671-89-1; **1c**, 19026-91-6; **2a**, 58790-01-5; **2b**, 88635-76-1; **3a**, 10474-24-5; **3b**, 88635-77-2; **3c**, 36628-80-5; **4a**, 4753-55-3; **4b**, 4759-11-9; **5**, 15825-93-1; **6**, 88635-78-3; **7**, 58853-55-7.

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