173. Electronic Structure and Photophysical Properties of Planar Conjugated Hydrocarbons with 4n-Membered Rings. I. Photoelectron Spectra of 1,5,9-Tridehydro[12]-annulene and Related Compounds

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(5. V. 76)

Summary. The HeI photoelectron spectra of the title compound **1** (1,5,9-cyclododecatriene-3,7,11-triyne), 1,5-didehydro[12]annulene (1,3,5,9-cyclododecatetraene-7,11-diyne (**2**)), *sym*-tribenzotridehydro[12]annulene (tribenzo[*a,e,i*]-5,6,11,12,17,18-hexadehydrocyclododecene (**3**)), and *sym*-dibenzodidehydro[8]annulene (dibenzo[*a,e*]-5,6,11,12-tetradehydrocyclooctene (**4**)) have been recorded and analysed on the basis of various semi-empirical model calculations. Despite the distinct bond length alternation in the parent compounds and, apparently, in the radical cations, the first ionization occurs at low energies in these compounds (7.6 ± 0.2 eV). The spectra yield little information with regard to the transannular interactions of the triple bonds.

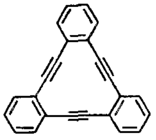
According to the well-known *Hückel* (4n + 2)-rule [1] cyclic conjugated hydrocarbons with 4n π-electrons are predicted to be unstable, open-shell species devoid of aromatic character. Despite the recent matrix-isolations of the long-sought parent compound, cyclobutadiene, its molecular symmetry and ground state multiplicity are still a matter of some controversy [2]. Higher [4n]annulenes are available [3] but they assume nonplanar equilibrium conformations due to geometric ring strain, nonbonded interactions, and possibly pseudo-*Jahn-Teller* distortions. Some bridged systems with essentially planar conjugated rings containing 4n π-electrons such as 1,7-methano[12]annulene [4] and the nonalternant hydrocarbons heptalene [5] and pyracylene [6] have been prepared. Alternatively, planarity in the higher annulenes may be enforced by the incorporation of triple bonds [3]. The equilibrium structures with alternating single and double bonds of the bridged [12]annulenes are stabilized by *ca.* 4 kcal/mol with respect to the delocalized transition states for their interconversion [4] [5]. This π-bond localization is enforced in most dehydroannulenes since the in-plane π'-bonds provide a bias favouring that valence structure with the greater number of formal triple bonds. Using either *Benson*'s group additivity tables [7] or the recent *ab initio* calculations on C_4 hydrocarbons by *Hehre* & *Pople* [8], the isomerization reaction but-1-en-3-yne → 1,2,3-butatriene is predicted to be endothermic by *ca.* 11 kcal/mol. Thus for 1,5,9-tridehydro[12]annulene the valence structure **1** is favoured over structure **1'** by *ca.* 33 kcal/mol, making it doubtful that the latter corresponds to a minimum on the potential surface.

1

1'

The pernicious effects of cyclic conjugation in [4n]annulenes predicted by MO theory are thus strongly tempered by bond alternation and one has to resort to highly sensitive probes such as NMR. chemical shifts [3] [9] in order to reveal any special attributes of 4n topology in the electronic ground state. The open-shell character of such systems does manifest itself by their ease of reduction to form stable radical anions and dianions [3] and by their long-wavelength electronic absorption spectra. Comparatively little is known about their radical cations [10] and dications [11].

2



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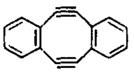

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We now report the photoelectron (PE.) spectra of the hydrocarbons **1** to **4** (Fig. 1) which are taken to have essentially planar equilibrium structures with alternating bond lengths in the 4n-membered ring. This presumption is established by X-ray structural data in the case of **3** [12] and **4** [13]. We note that the C≡C–C bond angles in **4** are distorted from linearity by a mean value of 24.2° as a result of the angle strain at the benzenoid rings and the transannular repulsion of the acetylene moieties (distance between the triple bonds 2.61 Å). No angle strain is present in **3** and the transannular interactions (distance between *ortho*-carbon atoms 2.86 Å) are insufficient to produce a significant distortion of the triple bonds. While it appears safe to assume a similar structure for **1**, the imputed planarity of **2** is much less obvious: Molecular models suggest that both bond angle strain and nonbonded repulsion of the inner *trans* double bond hydrogen atom are minimized in a conformation where the *trans* double bond is orthogonal to the rest of the ring. Furthermore, cyclic conjugation in the planar system should, if anything, be destabilizing [14]. However, the NMR. spectra of **2** and its 5-bromo derivative [15] provide strong evidence that the former rapidly equilibrates between two essentially planar conformers and this is supported by the near identity of the electronic absorption spectra of **1** and **2** [16].

The PE. spectrum of **1** down to 13 eV ionization energy consists of four well-separated features of which ② obviously results from several overlapping bands. The spectrum is readily interpreted on the basis of *Koopmans'* theorem using the simple LCBO (Linear Combination of Bonding Orbitals) model which has yielded accurate predictions of π-ionization potentials for a large body of planar poly-enes and -ynes [17]. Making use of symmetry (D_{3h}), the secular determinant for the out-of-plane π-system reduces to the two two-dimensional determinants (1).

$$A_2'': \begin{Vmatrix} A_d - \varepsilon & 2B_{dt} \\ 2B_{dt} & A_t - \varepsilon \end{Vmatrix} = 0; \qquad E'': \begin{Vmatrix} A_d - \varepsilon & B_{dt} \\ B_{dt} & A_t - \varepsilon \end{Vmatrix} = 0 \qquad (1)$$

The parameters used are those calibrated previously [17]: $A_d = \langle \pi_d | \mathcal{H} | \pi_d \rangle = -10.35$ eV (π_d = double bond two-centre π-orbital), $A_t = \langle \pi_t | \mathcal{H} | \pi_t \rangle = -11.15$ eV (π_t = triple bond two-centre π-orbital), and $B_{dt} = \langle \pi_d | \mathcal{H} | \pi_t \rangle = -1.14$ eV. The three in-plane π'-orbitals fall under the irreducible representations A_1' and E'. From a comparison with related compounds [17] they are expected to appear near 10 eV, *i.e.* within the broad feature ②. The vertical IP's are listed in Table 1 along with the results of the LCBO, SPINDO [18], MINDO/2 [19], MINDO/3 [20], PPP [21] models and of an $X\alpha$-calculation by *Boudreaux* [22]. The SPINDO, MINDO, and PPP calculations were made for idealized geometries using 'standard' [23] bond lengths. The bond angles in **4** were taken from [13]. The following parameters were used in the PPP SCF calculations: Valence state ionization potential $I_\mu = -10$ eV, one-centre electron repulsion integral $\gamma_{\mu\mu} = 10.48$ eV, two-centre electron repulsion integral $\gamma_{\mu\nu} = 14.399/(1.328 + r_{\mu\nu})$ eV ($[r_{\mu\nu}] = \text{Å}$), and an adjustable resonance integral $\beta_{\mu\nu} = -2.318 \exp (0.25 < p_{\mu\nu} - 2/3 >)$ eV where the calculated bond order $p_{\mu\nu}$ was increased by unity for the essential triple bonds and $\beta_{\mu\nu}$ was adjusted within the SCF-cycles. The qualitative agreement between the various models is not surprising as the π-orbitals of **1** are largely determined by symmetry.

The bands contained in ① to ④ are thus associated with the complete set of six out-of-plane π- and three in-plane π'-orbitals of **1** placing the σ-orbitals at energies below -13 eV. The narrow shape of the bands ③ and ④ lends support to their assignment to states of π-symmetry. Furthermore, the SPINDO-model yields an energy of -13.06 eV for the highest occupied σ-orbital, a value which deserves credit as an upper limit since for open-chain olefins [24] and acetylenes [17] the observed ionization energy attributed to the highest σ-orbital is consistently higher (*ca.* 0.5 eV) than that predicted by SPINDO on the basis of *Koopman*'s theorem. The bias of MINDO calculations to underestimate σ-ionization energies is well known.

The IP's assigned to ionization from the a_2'' π-orbitals, 7.69 and 12.4 eV, are predicted to lie at 8.44 and 13.06 eV by the LCBO-model. In view of its precision in related systems, the differences of 0.75 and 0.7 eV are noteworthy. One might argue that the basis energies A_d and A_t need to be corrected for the inductive effect due to the attached double or triple bonds. However, the inaccuracy is inherent to the LCBO-*Ansatz* (1), not to the choice of parameters: The means of either the two a_2'' or the four e'' orbital energies are predicted to equal $(A_d + A_t)/2$ while the means of the corresponding vertical IP's differ by 0.8 ± 0.1 eV. This discrepancy may be explained as follows: Since the LCBO-model does not allow for conjugative stabilization by mixing with antibonding orbitals, this effect must be absorbed in the calibrated basis energies A. Due to the high symmetry of **1**, the a_2'' orbitals cannot profit from such a stabilization because the basis spanned by the two-centre π^* orbitals does not contain the A_2'' representation. Hence, the corresponding ionization energies predicted with 'standard' parameters are too high. The first IP. of cyclobutadiene has been estimated as 8.5 [25], 8.4 [10c], and 8.2 eV [26]. Compared with IP_1 (**1**) these values appear to be too high. The LCBO-model (corrected as discussed above) yields the value $- A_d + 2B_{dd} - 0.8 = 7.3$ eV.

The first ionization band of **1** is narrow and structured, its first apparent vibrational peak being by far the most intense. This indicates that the bond length alternation of **1** largely persists in the ground state of its radical cation, presumably due to the presence of the in-plane π'-bonds. In contrast, the first PE. band of cyclobutadiene derivatives [10b–10d] is characteristic for a transition to a cation state with an equilibrium geometry differing markedly from that of the parent molecule.

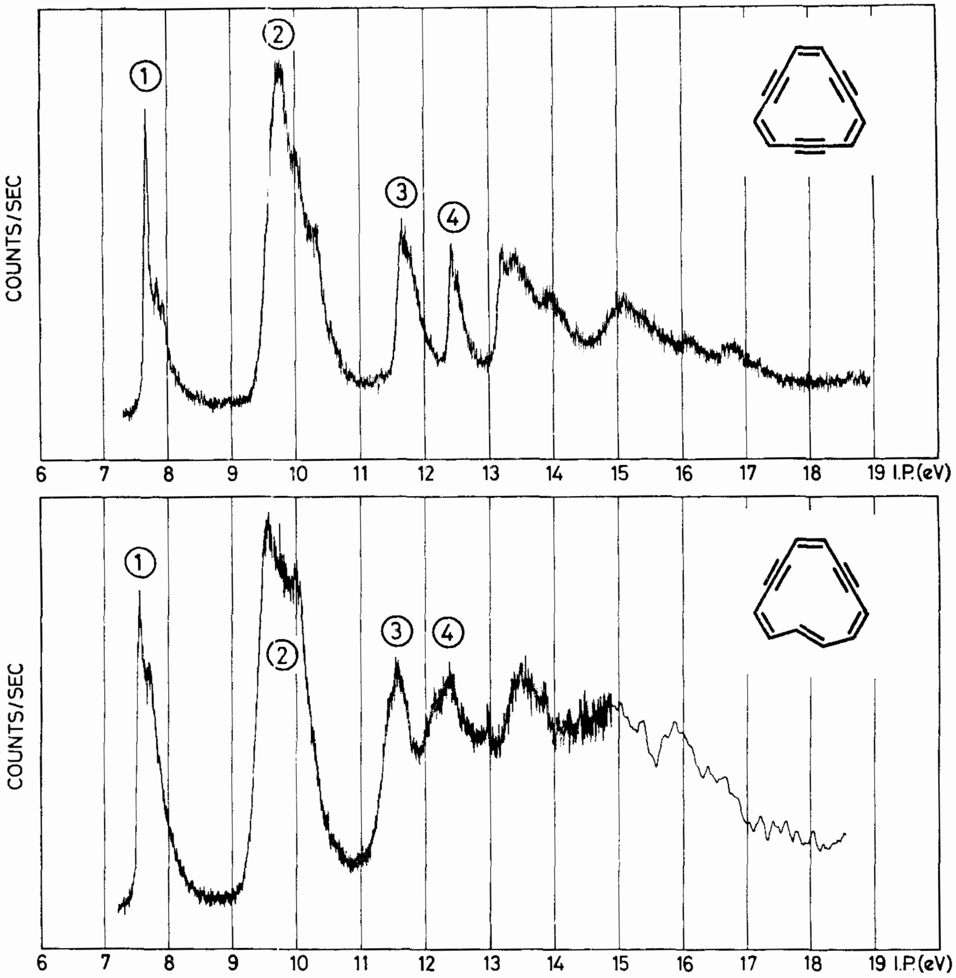


Fig. 1. *HeI PE spectra of* **1** *to* **4**

The calculated splitting between the in-plane π'-orbitals, $\varepsilon(5a_1) - \varepsilon(7e')$, amounts to only -0.02 and $+0.24$ eV in the SPINDO and MINDO/2 calculations, respectively, due to a near cancellation of 'through-space' and 'through-bond' interactions. From the interaction matrix between the three localized π'-orbitals, the splitting arising from 'through-space' interactions only [27] is predicted as $(-10.75) - (-10.21) = -0.54$ and $(-11.63) - (-10.49) = -1.14$ eV by the two models, respectively. Only an upper limit of $|\pm 0.6 \text{ eV}|$ can be given with certainty for the difference between the corresponding ionization energies because of the overlap with the $2e''$-band in feature ②, although a value of ~ 0.3 eV is probable from the high-energy structure of ②.

The spectrum of **2** (Fig. 1, Table 1) resembles that of **1** but it exhibits less fine structure and the first σ-ionization bands appear at lower energy. We may conclude that the equilibrium conformations of **2** are essentially planar in the gas phase also.

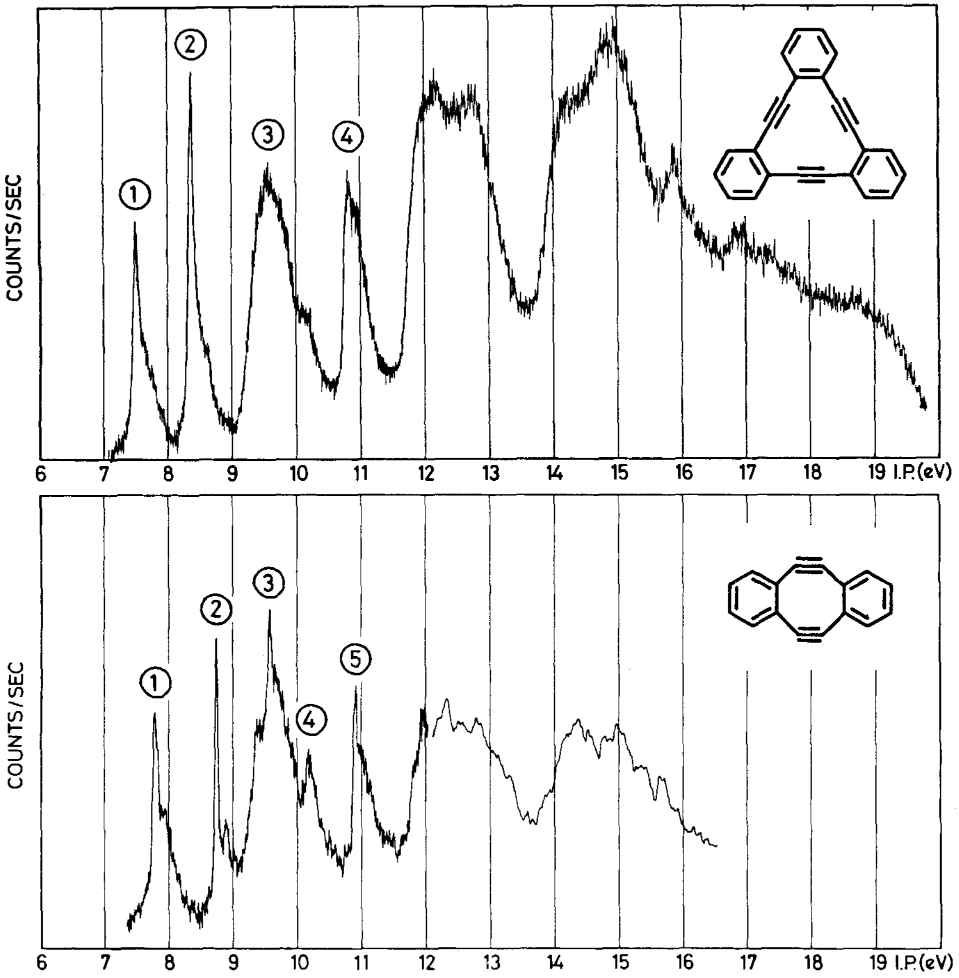


Fig. 1 (continued)

The predictions of an LCBO calculation in which the 9,10-double bond was removed from conjugation were incompatible with experiment ($\varepsilon_{\mathrm{HOMO}} = -8.74$ eV; $I_{v,1} = 7.54$ eV). Note, however, that the PE. spectrum is insensitive to 'small' ($< 30°$) deviations from planarity.

The assignments of the resolved bands in the spectra of **3** and **4** are straightforward (Table 1). Again, it is difficult to pin down the position of the π'-bonds within the broad features ③. Relying on the fairly consistent results of the LCBO, SPINDO, and PPP calculations we may tentatively associate the bonding ($9a_g$) and antibonding ($7b_{3u}$) combination of the in-plane π'-orbitals of **4** with the bands at 10.15 and ~ 9.7 eV, respectively. Once more, the substantial splitting due to the transannular 'through-space' interaction of the π'-bonds is largely annihilated by further mixing with the lower-lying σ-bonds: The symmetry-adapted localized π'-orbitals are located at -11.18 ± 0.74 eV by SPINDO while the corresponding canonical orbitals

Table 1. *Vertical ionization energies $I_{v,j}$ and calculated orbital energies $-\varepsilon_j$ [eV]*

		①	②			③	④								
	$I_{v,j}$	7.69	9.5	÷	10.4	11.67	12.4	13.2 ...							
	ψ_j	$2a_2''$	$2e''$	$7e'$	$5a_1'$	$1e''$	$1a_2''$	$6e'$	$2a_2'$	$5e'$	$4a_1'$	$3a_1'$	$4e'$	$3e'$...	
		π	π	π'	π'	π	π	σ	σ	σ	σ	σ	σ	σ	
	LCBO	8.44	9.54	—	—	11.96	13.06	—							
1	SPINDO	8.35	9.71	9.91	9.93	11.63	12.39	13.06	13.67	15.09	15.21	16.27	16.77	19.07	
	MINDO/2	8.07	9.82	9.79	9.55	12.30	13.37	10.42 a)	12.76 a)	13.45	11.88 a)	...			
	MINDO/3	7.49	9.50	9.72	9.53	12.17	13.29	11.07 a)	13.23 a)	14.00	12.56 a)	...			
	PPP	7.51	9.47	—	—	11.78	12.52	—							
	X_α	6.79	8.41	8.51	9.32	10.27	10.98	12.44	12.47	14.39	14.61	16.44	16.60	18.72	
		①	②				③		④						
	$I_{v,j}$	7.54	9.3	÷		10.4	11.5	11.7	12.2	12.4	...				
	ψ_j	6π	5π	4π	$2\pi'$	$1\pi'$	3π	2π	σ	2π					
2	LCBO	8.28	9.35	9.54	—	—	11.61	11.96	—	12.96	—				
	PPP	7.31	9.28	9.52	—	—	11.42	11.78	—	12.42	—				
		①	②	③				④							
	$I_{v,j}$	7.45	8.29	9.2	÷		10.2	10.76	~10.9	12.0	...				
	ψ_j	$3a_2''$	$4e''$	$1a_1''$	$3e''$	$14e'$	$9a_1'$	$2a_2''$	$2e''$		$1e''$	$1a_2''$			
3		π	π	π	π	π'	π'	π	π	σ	π	π			
	LCBO	8.21	8.69	9.25	9.25	—	—	11.08	11.32	—	12.64	13.35			
	PPP	7.80	8.61	9.37	9.48	—	—	10.91	11.22	—	12.61	13.12			
		①	②	③			④	⑤							
	$I_{v,j}$	7.76	8.74	9.3	÷	9.8	10.15	10.94	~11.0	12.0 ...					
	ψ_j	$3b_{1u}$	$2b_{2g}$	$1a_u$	$2b_{3g}$	$7b_{3u}$	$9a_g$	$2b_{1u}$	$1b_{2g}$	$7b_{2u}$	$8a_g$	$6b_{3u}$	$1b_{3g}$	$5b_{1g}$	$1b_{1u}$
		π	π	π	π	π'	π'	π	π	σ	σ	σ	π	σ	π
4	LCBO	8.21	8.87	9.25	9.25	—	—	11.08	11.53	—	—	—	12.25	—	13.35
	SPINDO	8.32	9.11	9.62	9.69	9.92	10.20	11.05	10.98	12.16	12.34	12.36	12.64	12.69	13.16
	MINDO/2	8.21	9.08	9.76	9.90	8.90 a)	9.18 a)	11.51	11.33	10.32 a)	10.21 a)	9.96 a)	13.54	10.61 a)	14.34
	PPP	7.88	8.77	9.37	9.54	—	—	10.91	11.46	—	—	—	12.31	—	13.11

a) Orbital sequence interchanged relative to corresponding band positions.

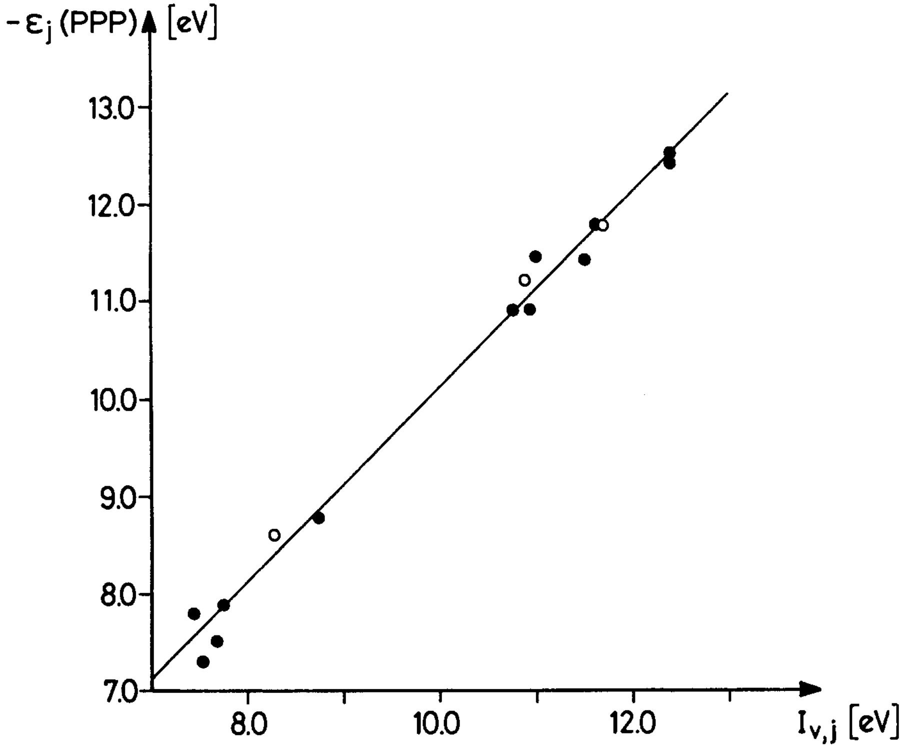


Fig. 2. *Experimental ionization potentials $I_{v,j}$ versus PPP SCF orbital energies.* Uncertain IP's in the region of overlap with π'-bands (10 ± 0.5 eV) are omitted. Circled points (○) for degenerate orbitals were weighted by a factor of two

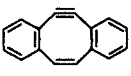
are shifted to −10.20 ($9a_g$) and −9.92 eV ($7b_{3u}$). A detailed analysis for the closely related case of 1,5-cyclooctadiyne is given in [28].

In order to quantify the reliability of the calculated π-band positions in the region of overlap with the π'-bands, their 90 percent confidence ranges were determined from a variance analysis of the linear regression shown in Fig. 2 between 18 resolved vertical IP's of **1** to **4** (independent variable) and the corresponding PPP orbital energies (dependent variable). A least-squares calculation for the trial function

$$-\varepsilon_j = A + B \cdot I_{v,j} \qquad (2)$$

yields the parameters $A = 0.07 \pm 0.58$ ($P_d = 0.1$), $B = 1.006 \pm 0.046$ ($P_d = 0.1$) with $r = 0.995$ and a residual variance of 0.039 eV^2 about the regression. Hence, the 90 percent confidence ranges for the prediction of unknown IP's of **1** to **4** in the range of 10 ± 2 eV may be estimated as

$$I_{v,j} = -\frac{\varepsilon_j + A}{B} \pm 0.36 \text{ eV}. \qquad (3)$$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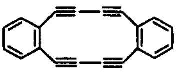
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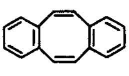
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Finally, it should be mentioned that attempts were also made to record the PE. spectra of dibenzo[*a, e*]-5,6-didehydrocyclooctene (**5**) [29] and dibenz[*a, g*]-5,6,7,8,13,14,15,16-octadehydrocyclododecene (**6**) [30] both of which did not yield a sufficient vapour pressure below their temperature of decomposition. Spectra of minor quality obtained with **5** were similar to that of **4**, the first two vertical IP's of **5** lying at 7.5_6 and 8.5_6 eV. As expected, the spectrum of dibenzo[*a, e*]cyclooctene (**7**) differs strongly from those of **4** and **5**. Due to the non-planarity of **7** the ionization bands are broad and the first maximum is shifted to higher energy ($I_{v,1} = 8.24$ eV, apparent onset at *ca.* 7.8 eV).

Experimental Part. – The HeI photoelectron spectra were recorded on a modified *Perkin-Elmer* PS 16 instrument. The samples were inserted directly in the vicinity of the ionization region which was heated to temperatures of 55° (**1**, **2**), 205° (**3**), 85° (**4**), and 77° (**7**). The ionization energies were determined by an *in situ* calibration with benzene and rare gases.

Tridehydro[12]annulene (**1**) was synthesized by the procedure of *Untch & Wysocki* [31]. The final dehydrobromination was, however, effected with potassium *t*-butoxide in THF whereby the didehydro[12]annulene (**2**) [16] was formed as a by-product of **1** in *ca.* 20 percent yield.

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174. A ^{13}C- and ^{15}N-NMR. Study of Some 1-Aryl-3,3-dimethyl Triazene Derivatives

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Summary. ^{13}C- and ^{15}N-NMR. spectra have been measured for a series of triazenes. The results are compatible with the significant contribution of a structure such as II. One-bond nitrogen-nitrogen coupling constants are reported.

There is a relatively widespread distribution of molecules containing nitrogen in which this heteroatom is involved in an extended π-system. In these cases it is possible that there is a considerable delocalization of charge density from (or to) the nitrogen from other atoms in the system. Triazenes of type **1** represent one such class of molecules. For a wide variety of X-groups, a dipolar structure, such as **2**, is thought [1] to be important. Indeed, variable temperature ^{1}H-NMR. studies have already demonstrated [1] that restricted rotation exists about the N(2)–N(3) 'single' bond. While ^{1}H-NMR. has shown that the methyl groups of **1** are not equivalent it is interesting to ask whether or not this non-equivalence stems only from **2** or whether a structure such as **3** makes a major contribution since, in both structures, alkyl groups on the amino-nitrogen would lie in magnetically non-equivalent sites. Since **3** implies a change in the nature of the carbon π-system, whereas **2** results primarily from changes at the nitrogen centers, a combined ^{13}C- and ^{15}N-NMR. study should be valuable as both of these forms of magnetic resonance are capable of monitoring changes in charge density at the nuclear center. To further this end we have synthesized and measured the ^{15}N-(I = 1/2, natural abundance = 0.36%) and ^{13}C-NMR. characteristics of two series of such triazenes with one set containing ^{15}N (greater than 95 atom % ^{15}N) at positions N(1) and N(2) and a second set enriched at positions N(2) and N(3).

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