54. The Low-Temperature UV/VIS Absorption Spectrum of [14]Annulene

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The UV/VIS absorption spectrum of [14]annulene was measured in 3-methylpentane at room and liquid-N_2 temperatures and interpreted by the CNDO/S-CI method. This comparison between experiment and theory supports a structure with π-bond delocalization for this molecule.

Introduction. – [14]Annulene, a compound crystallizing as brown needles, was synthesized in 1960 by *Sondheimer* and *Gaoni* [1]. A preliminary X-ray study performed by *Bregman* [2] indicated a structure with a distorted pyrene perimeter for this molecule. A more extensive X-ray study, realized in 1972 [3], confirmed *Bregman*'s [2] preliminary study and concluded that the molecular structure has its π-bonds delocalized and belongs to the C_i symmetry group. The UV/VIS absorptions in isooctane were reported by *Sondheimer* and *Gaoni* [1] as follows: maxima at 31850 (ε = 69000) and at 26740 cm^{-1} (ε = 5700). This UV/VIS spectrum was interpreted by *Blattmann et al.* [4]: on the basis of a PPP calculation, these authors demonstrated the correlation existing between the reported transitions of [14]annulene and those of benzene and of [18]annulene. One year later, *Trinajstić* and *Wratten* [5] considered the agreement between the theoretical and experimental spectrum of the title compound as very poor, stating that this poor agreement 'indicates that the PPP method may not be applicable to this important class of conjugated molecules' [5]. They were led to such a conclusion due to their ignorance of the existence of a transition at *ca.* 16000 cm^{-1} which was not observed and thus not reported in [1].

To interpret the PE spectrum of [14]annulene measured by one of us (*J.F.M.O.*), the geometry of the molecule was optimized by the MINDO/2 method [6]. This geometry showed π-bonds localized, a finding which was later reproduced by MINDO/3 calculations performed by *Vogler* [7]. Such a geometry with localized π-bonds was for us in contradiction with other spectroscopic data (NMR dynamics and IR spectrum) as was also in doubt the MINDO/3-optimized geometry (with π-bonds localized) obtained by *Dewar et al.* for [18]annulene [8]. The fact that the MINDO method leads to π-bond-localized structures for [14] and [18]annulene was explained by one of us [9] [10]: it was shown that configuration interactions between doubly excited states and the ground state, when correctly taken into account, favor π-bond delocalization. Molecular-mechanics computations were shown to also predict π-bond localization for [18]- but π-bond delocalization for [14]annulene [11].

In a review on the conformational mobility and π-bond shift in the annulenes, *Oth* [12] reported NMR investigations of this molecule [13]. According to this study, *Scheme*

[14]-43-annulene [14]-21-annulene

[14]annulene exists in solution as an equilibrium mixture of two isomers differing by their configurations, namely the [14]-43- and the [14]-21-annulene (for the coding of the configuration, see [12] and *Scheme*). The [14]-43-annulene was shown to be the major component in solution, while it is the only species observed in the crystal. From the chemical shifts of the protons pointing inside the ring, it was concluded that the [14]-43-annulene most likely has its π-bonds delocalized, although the perimeter must be appreciably distorted from a planar geometry, as result of the steric interactions between the four inner protons; it was not possible to decide if the [14]-21-annulene has its π-bonds localized or delocalized but certainly the ring, in this configuration, must be strongly puckered. *Haddon* [14] [15] interpreted the ^{1}H-NMR chemical shifts on the basic of ring-current calculations and pointed out that the nonplanarity of the π-perimeter as well as π-bond localization could explain the δ(H)'s reported by *Oth* [12]. Other computations of the ring current, taking into account local anisotropies, performed by *Vogler* [7], led to the conclusion that a structure with π-bond localization has to be rejected.

In the last decade, several books and reviews on annulenes in general and the different [14]annulenes in particular have appeared in connection with the concept of aromaticity, new synthetic approaches, and measured and computed physical properties of these compounds [16]. *Vogel* and coworkers published the synthesis and properties of *syn*-1,6-ethano-8,13-methano[14]annulene [17], *syn*-1,6-imino-8,13-methano[14]annulene [18], a large number of different methano-bridged [14]annulenes [19], *anti*-1,6:8,13-bismethano[14]annulene-15,16-dione [20], *syn*-1,6:8,13-bismethano[14]annulene-15,16-dione [21], an exceptional oxidative transformation of nonbenzenoid aromatic isoprene giving [14]annulenes with an anthracene perimeter [22], and the synthesis of *syn*-1,6-imino-8,13-oxido[14]annulene [23]. *Müllen* and coworkers reported the synthesis and properties of *trans*-15,16-dimethyl-1,4:8,11-ethanediylidene[14]annulene [24], and dialkyl- and dihydro derivatives of dicyclopenta[*ef*,*kl*]heptalene [25]. *Hafner et al.* described two major synthetic approaches to bridged [4*n* + 2]annulenes with a naphthalene or an acene perimeter [26], and the synthesis of a dicyclopenta[*a*,*e*]pentalene [27]. *Gazit* [28] proposed a general and efficient route to bridged dibenzo[14]annulene-quinones which affords easily available precursors for the preparation of [14]annulene. *Ojima et al.* reported the synthesis and properties of dibenzo-annelated [14]annulenes [29] and of α-alkyl-substituted didehydroaza[14]annulenes and the related benzo-annelated derivatives [30]. *Leaver* [31] published the synthesis and characterization of cycloazines and related N-bridged annulenes, among these pyrazino[2,1,6-*cd*:5,4,3-*c*′*d*′]dipyrrolizine. *Meissner et al.* [32] synthesized naphth[1,2-*a*]- and -[2,3-*a*][14]annulene.

Vogel and coworkers studied by NMR the dynamic behavior of *syn*-1,6-ethano-8,13-methano[14]annulene [33] and of *syn*-1,6:8,13-diimino[14]annulene [34]. *Müllen* and coworkers, by the same method, studied the kinetics of the reduction of a homologous series of *Nakagawa*-type annulenes [35] and various dianions and dications derived from bridged [14]annulenes [36].

X-Ray studies were published by *Vogel* and coworkers of the *syn*-1,6:8,13-diimino[14]annulenes with and without bridge connection [37] and in combination with CD spectroscopy for the determination of the absolute configurations of bridged [14]annulenes [38].

A fascinating chapter of the [14]annulene chemistry started in 1975 with the synthesis of a tetraaza compound by *L'Eplattenier* and *Pugin* [39]. *Nalwa* and *Kakuta* [40] recently reviewed the organometallic *Langmuir-Blodgett* films and their importance for electronics and photonics. As further examples in this field, we mention *Honeybourne* and coworkers who investigated dihydrodibenzo[*b,i*][1,4,8,11]tetraazacyclotetradecine and its dark DC conductivity and spectroscopy of clean and gas-doped thin films [41], performed acousto-electrical and surface plasmon resonant responses from NOX-doped *Langmuir-Blodgett* (*L–B*) films of macrocycles [42], and studied gas-surface interactions with *L–B* films of new derivatives of dihydrotetraazadibenzo[14]annulenes [43], and films of metal-free [1,4,8,11]tetraaza[14]annulene [44]. *Limbach et al.* observed a non-concerted double proton transfer in the solid state of a tetramethyldibenzotetraaza[14]annulene [45] which they studied by high-resolution solid-state NMR relaxometry [46].

The quantitative electrophilic reactivity of the [14]annulenes was studied by *Laws* and *Taylor* [47].

Quantum-chemical computations were done by *Destro et al.* [48] comparing the X-ray structures of *syn*-1,6:8,13-diimino[14]annulenes with connected bridges to their MINDO/3 computed geometries, by *Vogler* and *Mitchell* computing by the π-SCF force-field method ^{1}H-NMR chemical shifts and geometries of [14]annulenes and their dianion salts [49], as well as of dihydropyrene and several of its benzo-annelated derivatives [50], and by *Cremer et al.* [51] investigating the configurational stability of oxido-bridged [14]annulenes by HF/STO-3G, HF/4-31G, MP2/STO-3G, MNDO and correlation-corrected MNDO calculations. *Stollenwerk et al.* [52] computed magnetic susceptibilities and topological resonance energies (TRE) of annelated [14]annulenes, *Favini et al.* [53] studied some new bridged [14]annulenes by empirical force-field calculations, *Loos* and *Leska* [54] used EHT, CNDO/2, MINDO/2, and empirical potentials for the calculation of the geometry of six isomers of [14]annulene, *Hernando et al.* [55] made an AM1 study of the interconversion of the isomers of [14]annulene, and *Vogel* and coworkers [56] investigated the existence of a thermal equilibrium between aromatic *syn*-1,6:8,13-bisoxido-[14]annulene and its olefinic *anti*-isomer by the MNDO- and STO-3G/HF methods.

In spite of that large number of interesting papers, the low-temperature UV/VIS absorption spectrum of [14]annulene has not yet been published, and in this paper we present the UV/VIS absorption spectrum of [14]annulene measured in 3-methylpentane at room and at liquid-N_2 (glass) temperatures and the interpretation of the observed transitions based on CNDO/S-CI [57] [58] calculations. The CNDO/S-CI calculations were performed using different possible geometries with and without π-bond delocalization, to be able to conclude what the actual π-bond situation is in the [14]-43-annulene.

Experimental. – The [14]annulene was synthesized according to the procedure reported in [1]. The UV/VIS spectra were measured at room and liquid-N_2 temperatures in 3-methylpentane (see *Fig. 1*) using a *Cary-17* spectrometer and a home-made cryostat equipped with a 1-cm cell. The first weak absorption band in the region of 600 nm was measured with a $1.92 \cdot 10^{-3}$ M solution, while the rest of the spectrum was recorded with a 100-fold diluted solution. The first absorption band shows an extensive vibrational fine structure; its rather strong $(0 \leftarrow 0)$ component at 628 nm ($\log \varepsilon = 2.20$) implies a low symmetry for the molecule.

Interpretation. – *The Molecular Geometries Used. X-Ray Geometry.* According to the X-ray diffraction study, the [14]annulene molecule in the crystalline state has the 43 configuration [3] with its π-bonds delocalized, although the perimeter is considerably distorted from a planar form; the molecule belongs to the point group C_i. This molecular geometry is reproduced in *Fig. 2* and was used as starting point for the MINDO/3-optimized [59] geometries discussed below.

MINDO/3-Optimized Geometry of [14]-43-Annulene with π-Bonds Delocalized and Localized. We performed MINDO geometry optimizations for several π-bond situations. The geometry corresponding to the lowest calculated heat of formation (132.4 kcal/mol) is non-planar and has C_i symmetry; it is reproduced in *Fig. 3*. Allowing π-bond fixation, the MINDO/3 procedure leads to a structure with alternating double bonds and with symmetry C_s as the most stable structure (heat of formation: $\Delta H_f = 115.4$ kcal/mol). This structure is reproduced in *Fig. 4*. The fact that the MINDO/3 method favors this structure results from the neglect of electron correlation terms; as mentioned in the *Introduction*, the inclusion of configuration interaction in the MINDO method leads in fact to the opposite result, namely that the structure with delocalized π-bonds is more stable than the π-bond-localized one (see *Table 1*).

MINDO/3-Optimized Geometries of [14]-21-Annulene with π-Bonds Delocalized and Localized. MINDO/3 Optimization of the geometry of the 21-configuration leads to a π-bond-delocalized structure (*Fig. 5*) with a computed heat of formation of 133.1 kcal/mol, whereas the optimized π-bond-localized structure has a heat of formation of 110.9 kcal/mol, *i.e.*, *ca.* 20 kcal/mol lower in energy (*Fig. 6*; see *Table 1*).

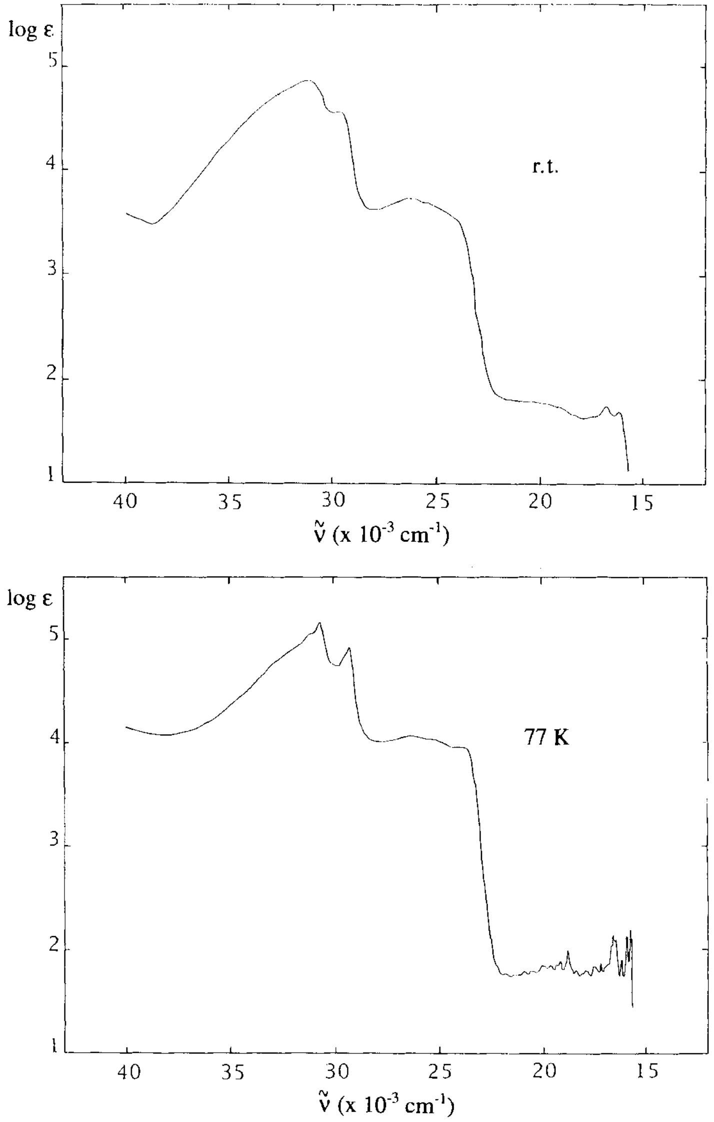


Fig. 1. *UV/VIS Spectrum of [14]annulene at r.t. and liquid-N_2 temperature*

	r [Å]		α [°]		Θ [°]
C(1)–C(2)	1.407	C(1)–C(2)–C(3)	125.5	C(1)–C(2)–C(3)–C(4)	162.7
C(2)–C(3)	1.350	C(2)–C(3)–C(4)	130.3	C(2)–C(3)–C(4)–C(5)	–162.5
C(3)–C(4)	1.382	C(3)–C(4)–C(5)	123.3	C(3)–C(4)–C(5)–C(6)	1.5
C(4)–C(5)	1.395	C(4)–C(5)–C(6)	125.2	C(4)–C(5)–C(6)–C(7)	162.0
C(5)–C(6)	1.356	C(5)–C(6)–C(7)	129.5	C(5)–C(6)–C(7)–C(8)	–164.9
C(6)–C(7)	1.381	C(6)–C(7)–C(8)	124.1	C(6)–C(7)–C(8)–C(9)	15.4
C(7)–C(8)	1.376	C(7)–C(8)–C(9)	128.4	C(7)–C(8)–C(9)–C(10)	13.1

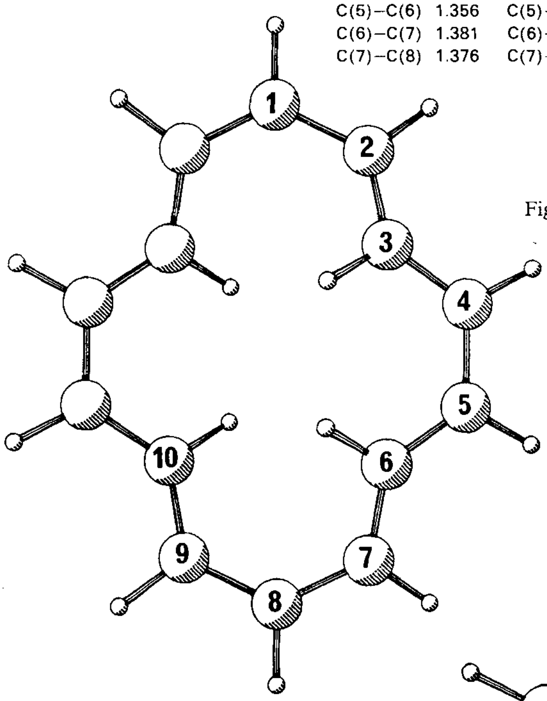
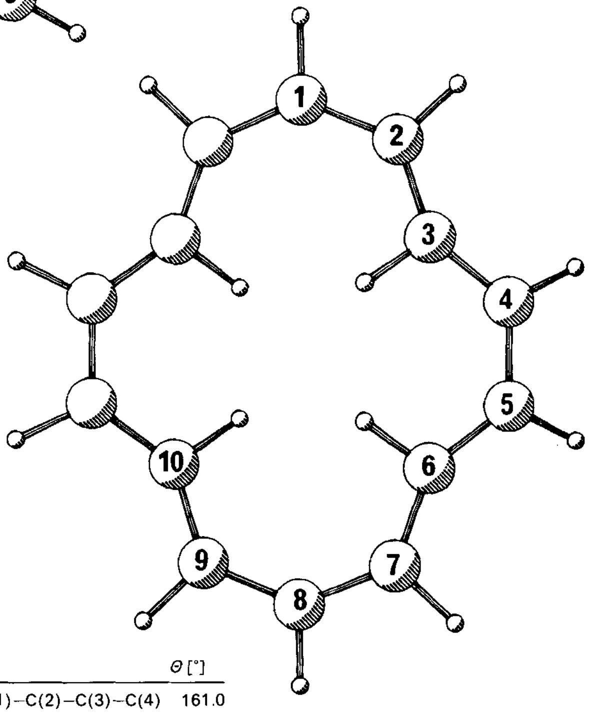


Fig. 2. *X-Ray structure of [14]annulene of symmetry* C_i



	r [Å]		α [°]		Θ [°]
C(1)–C(2)	1.410	C(1)–C(2)–C(3)	129.8	C(1)–C(2)–C(3)–C(4)	161.0
C(2)–C(3)	1.399	C(2)–C(3)–C(4)	142.2	C(2)–C(3)–C(4)–C(5)	–166.8
C(3)–C(4)	1.398	C(3)–C(4)–C(5)	127.0	C(3)–C(4)–C(5)–C(6)	–0.3
C(4)–C(5)	1.403	C(4)–C(5)–C(6)	126.2	C(4)–C(5)–C(6)–C(7)	166.5
C(5)–C(6)	1.402	C(5)–C(6)–C(7)	143.1	C(5)–C(6)–C(7)–C(8)	–151.9
C(6)–C(7)	1.396	C(6)–C(7)–C(8)	132.1	C(6)–C(7)–C(8)–C(9)	–6.4
C(7)–C(8)	1.401	C(7)–C(8)–C(9)	134.1	C(7)–C(8)–C(9)–C(10)	14.4

Fig. 3. *MINDO/3-Optimized structure of [14]-43-annulene of symmetry* C_i

	r [Å]		α [°]		θ [°]
C(1)–C(2)	1.478	C(1)–C(2)–C(3)	125.1	C(1)–C(2)–C(3)–C(4)	–170.4
C(2)–C(3)	1.355	C(2)–C(3)–C(4)	127.3	C(2)–C(3)–C(4)–C(5)	71.7
C(3)–C(4)	1.482	C(3)–C(4)–C(5)	125.2	C(3)–C(4)–C(5)–C(6)	–5.7
C(4)–C(5)	1.354	C(4)–C(5)–C(6)	123.1	C(4)–C(5)–C(6)–C(7)	–120.3
C(5)–C(6)	1.476	C(5)–C(6)–C(7)	123.7	C(5)–C(6)–C(7)–C(8)	156.4
C(6)–C(7)	1.355	C(6)–C(7)–C(8)	127.3	C(14)–C(1)–C(2)–C(3)	–130.8
C(7)–C(8)	1.483	C(14)–C(1)–C(2)	126.7		
C(1)–C(14)	1.340				

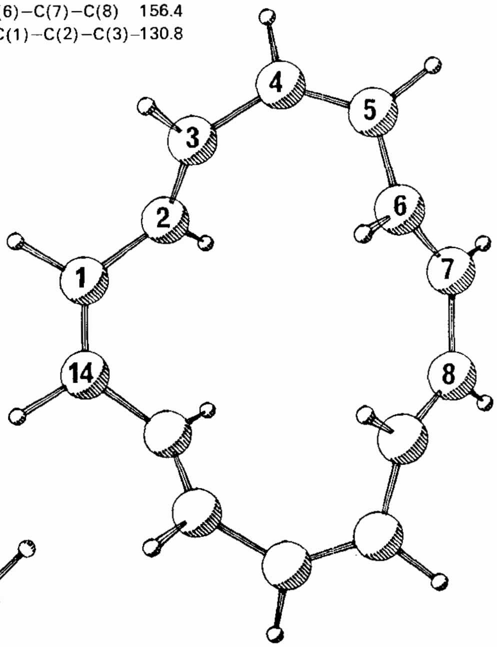
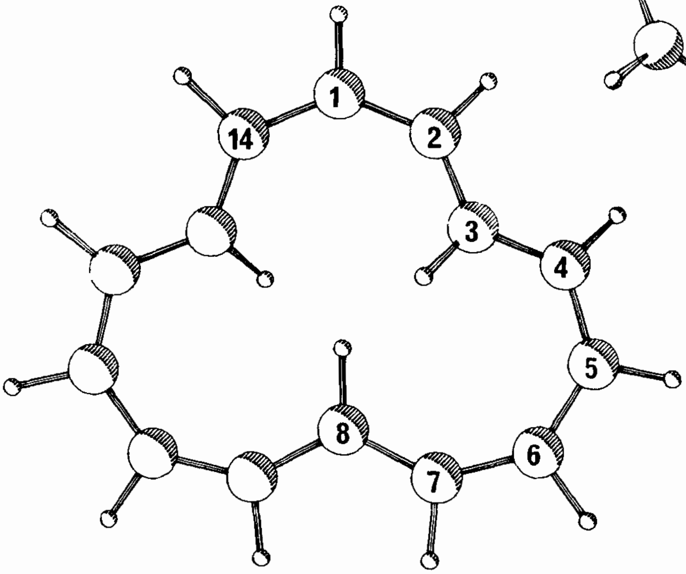
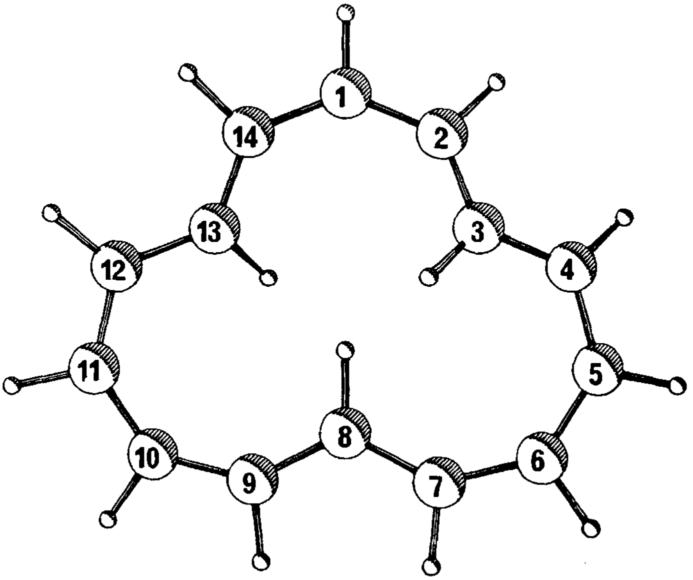


Fig. 4. *MINDO/3-Optimized structure of [14]-43-annulene of symmetry* C_s



	r [Å]		α [°]		θ [°]
C(1)–C(2)	1.400	C(1)–C(2)–C(3)	131.2	C(1)–C(2)–C(3)–C(4)	170.9
C(2)–C(3)	1.391	C(2)–C(3)–C(4)	128.3	C(2)–C(3)–C(4)–C(5)	–174.0
C(3)–C(4)	1.403	C(3)–C(4)–C(5)	123.5	C(3)–C(4)–C(5)–C(6)	17.0
C(4)–C(5)	1.399	C(4)–C(5)–C(6)	132.5	C(4)–C(5)–C(6)–C(7)	4.2
C(5)–C(6)	1.403	C(5)–C(6)–C(7)	137.0	C(5)–C(6)–C(7)–C(8)	–5.5
C(6)–C(7)	1.397	C(6)–C(7)–C(8)	139.1	C(6)–C(7)–C(8)–C(9)	176.0
C(7)–C(8)	1.404	C(7)–C(8)–C(9)	125.8	C(14)–C(1)–C(2)–C(3)	–14.3
		C(14)–C(1)–C(2)	141.3		

Fig. 5. *MINDO/3-Optimized structure of [14]-21-annulene of symmetry* C_2



	r [Å]		a [°]		Θ [°]
C(1)–C(2)	1.355	C(1)–C(2)–C(3)	131.2	C(1)–C(2)–C(3)–C(4)	168.5
C(2)–C(3)	1.456	C(2)–C(3)–C(4)	129.3	C(2)–C(3)–C(4)–C(5)	–174.0
C(3)–C(4)	1.354	C(3)–C(4)–C(5)	124.1	C(3)–C(4)–C(5)–C(6)	20.6
C(4)–C(5)	1.464	C(4)–C(5)–C(6)	133.3	C(4)–C(5)–C(6)–C(7)	4.5
C(5)–C(6)	1.358	C(5)–C(6)–C(7)	140.0	C(5)–C(6)–C(7)–C(8)	–6.7
C(6)–C(7)	1.467	C(6)–C(7)–C(8)	137.1	C(6)–C(7)–C(8)–C(9)	–179.0
C(7)–C(8)	1.355	C(7)–C(8)–C(9)	129.2	C(7)–C(8)–C(9)–C(10)	170.5
C(8)–C(9)	1.462	C(8)–C(9)–C(10)	133.8	C(8)–C(9)–C(10)–C(11)	–7.4
C(9)–C(10)	1.362	C(9)–C(10)–C(11)	141.6	C(9)–C(10)–C(11)–C(12)	9.5
C(10)–C(11)	1.465	C(10)–C(11)–C(12)	135.6	C(10)–C(11)–C(12)–C(13)	13.7
C(11)–C(12)	1.357	C(11)–C(12)–C(13)	124.0	C(11)–C(12)–C(13)–C(14)	–173.0
C(12)–C(13)	1.458	C(12)–C(13)–C(14)	129.2	C(12)–C(13)–C(14)–C(1)	170.3
C(13)–C(14)	1.355	C(13)–C(14)–C(1)	131.0	C(13)–C(14)–C(1)–C(2)	–19.0
C(1)–C(14)	1.455	C(14)–C(1)–C(2)	134.9	C(14)–C(1)–C(2)–C(3)	–9.9

Fig. 6. *MINDO/3-Optimized structure of [14]-21-annulene of symmetry* C_l

Table 1. *ΔH_f and Number of Considered Singly and Doubly Excited Electronic Configurations for Different Geometrical Configurations and Conformations of [14]Annulene*

Configuration	Geometry	Symmetry	π-Bonds	ΔH_f		Depression CI [10] with (number) doubly excit.	Number of configuration CNDO/S-CI	
				MINDO/3	MINDO/2		singly excited	doubly excited
43	*Fig. 3*	C_i	deloc.	132.4	143.8	110.7 (6472)	56	
							54	45
	Fig. 4	C_s	loc.	115.4	132.8	73.2 (8860)	69	
21	*Fig. 5*	C_2	deloc.	133.1	–	–	59	
							54	45
	Fig. 6	C_1	loc.	110.9	–	–	75	

Computation of the UV/VIS Transitions with the CNDO/CI Method [57] [58]. With the four geometries presented in *Figs. 3–6*, we computed the electronic transitions using the CNDO/S-CI method [57] [58]. *Table 1* reproduces the number of singly and doubly excited configurations taken into account for these computations. All the singly excited configurations considered lie less than 10 eV above the ground state (see *Tables 2–4*). For

Table 2. *Computed UV/VIS Transitions* (Geometry of *Fig. 3*)

Transition	Symmetry	ΔE [cm^{-1}]	Oscillator strength
1	A_u	15856	0.002
2	A_u	21709	0.005
3	A_u	31968	0.972
4	A_u	33434	1.558
5	A_g	37222	0
6	A_g	37728	0
7	A_u	38098	0.167
8	A_u	38888	0.239
9	A_g	43096	0

Table 3. *Computed UV/VIS Transitions* (Geometry of *Fig. 4*)

Transition	Symmetry	ΔE [cm^{-1}]	Oscillator strength
1	A''	32404	0.076
2	A'	37069	0.015
3	A'	38210	0.117
4	A''	40082	0.567
5	A'	41731	0.008
6	A'	42482	0.016
7	A''	44115	0.014
8	A'	44557	0.117
9	A''	44678	0.001

Table 4. *Computed UV/VIS Transitions* (Geometry of *Fig. 5*)

Transition	Symmetry	ΔE [cm^{-1}]	Oscillator strength
1	B	16297	0.000
2	A	21884	0.002
3	A	32155	0.968
4	B	33243	1.364
5	B	36596	0.081
6	A	36680	0.000
7	B	38100	0.077
8	B	40753	0.001
9	A	43984	0.007

Table 5. *Computed UV/VIS Transitions* (Geometry of *Fig. 3*) *Including Doubly Excited Configurations*

Transition	Symmetry	ΔE [cm^{-1}]	Oscillator strength
1	A_u	18546	0.002
2	A_u	25523	0.005
3	A_g	32308	0
4	A_g	32677	0
5	A_g	34212	0
6	A_u	34621	1.038
7	A_g	35125	0
8	A_u	35903	1.572
9	A_g	37919	0
10	A_g	38501	0
11	A_g	40561	0
12	A_g	40889	0
13	A_g	42726	0
14	A_u	43608	0.129
15	A_u	44212	0.198

Table 6. *Computed UV/VIS Transitions* (Geometry of *Fig. 5*) *Including Doubly Excited Configurations*

Transition	Symmetry	ΔE [cm^{-1}]	Oscillator strength
1	B	18841	0.000
2	A	25336	0.003
3	B	32227	0.002
4	A	32308	0.000
5	A	34491	0.211
6	B	34705	0.075
7	A	35053	0.809
8	B	35938	1.385
9	A	38431	0.008
10	B	38483	0.021
11	B	39792	0.043
12	A	40378	0.000
13	A	42915	0.001
14	B	43542	0.022
15	A	46144	0.000

the two structures with delocalized π-bonds, additional computations were performed, taking into consideration 54 singly and 45 doubly excited configurations (see *Tables 5* and *6*). The transition moments were computed as dipole vectors with all the simplifications following from the ZDO assumption. The results of some of these calculations (see also *Tables 2–6*) are compared with the experimental spectra in *Figs. 7* and *8*.

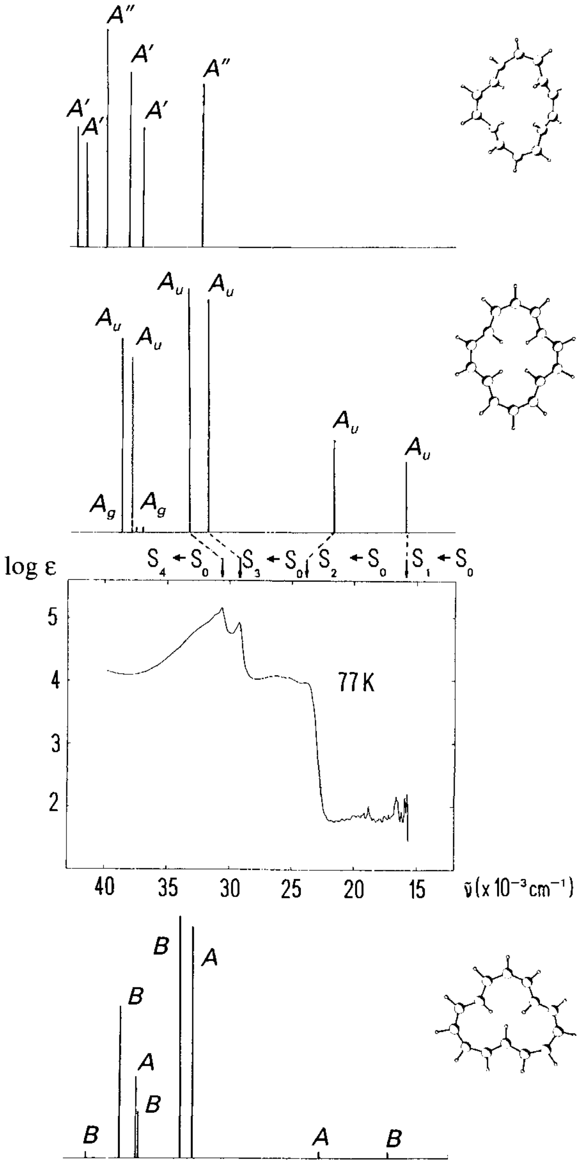


Fig. 7. *Comparison of the CNDO/S-CI spectra computed with π-bond-localized (C_s) and π-bond-delocalized (C_i, C_2) structures with the experimental results* (only singly excited configurations)

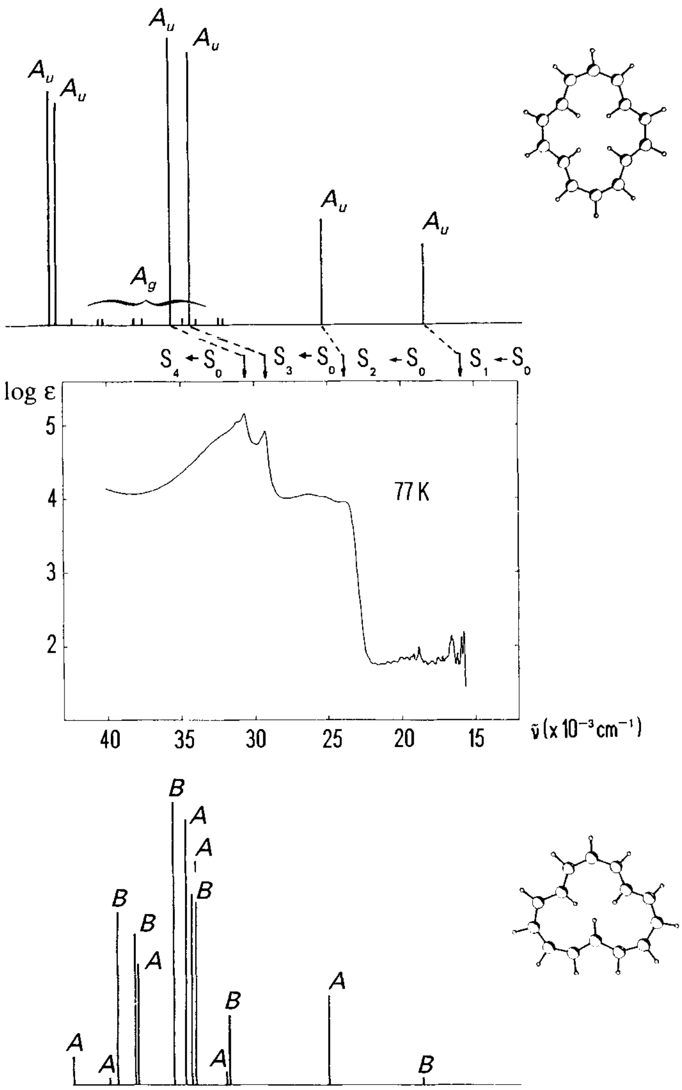


Fig. 8. *Comparison of the CNDO/S-CI spectra of the [14]-43-(C_i) and the [14]-21-annulene (C_2) with the experimental results* (singly and doubly excited configurations considered)

As can be seen, only the structures with delocalized π-bonds (C_i and C_2; *Figs. 3* and *5*, resp.) lead to theoretical transitions which are compatible with the experimental spectrum (*Fig. 7*). However, as in [18]annulene [60], the positions of the three characteristic transitions $S_1 \leftarrow S_0$, $S_2 \leftarrow S_0$, and $S_3 \leftarrow S_0$ are not perfectly reproduced. The introduction of the doubly excited configurations in the CI term improves the agreement between the computed and observed position of the transitions (*Fig. 8*), since it affects the relative positions of the states as illustrated in *Fig. 9*. From a structure with the π-bonds localized

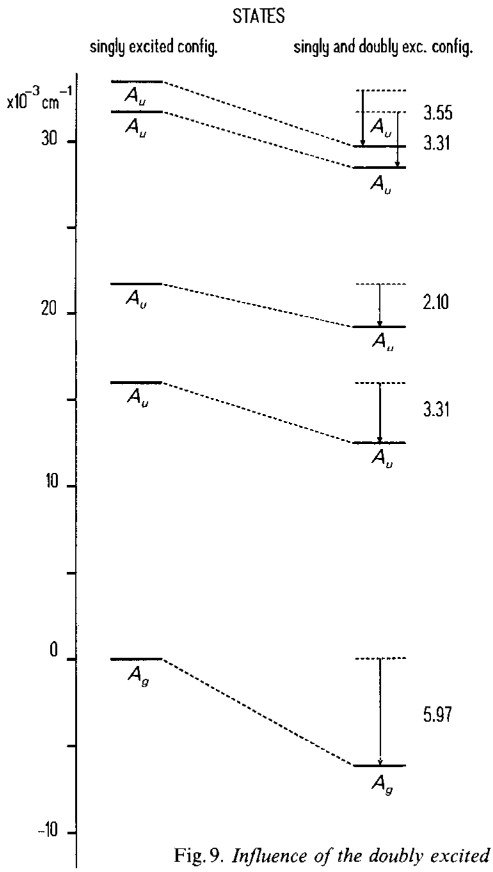


Fig. 9. *Influence of the doubly excited configurations on the energies of the S_1, S_2, and S_3 states of [14]annulene with* C_i *symmetry*

(*Fig. 4*), one computes the first transition at 32400 cm^{-1} which does not correspond to any observed transitions. In the low-temperature spectrum (see *Fig. 1*), one can see absorptions at *ca.* 19000 cm^{-1}. This transition from the ground state to a 'phantom state' (also called 'mystery band' or 'A band') was also observed by *Blattmann et al.* [4] and *Kolc et al.* [61] for different molecules having a [14]annulene perimeter and further for anthracene by *Hohlneicher* and *Dick* [62] who used the CNDO/S method with inclusion of the doubly excited configurations as earlier proposed by one of us (*H.B.*) for the interpretation of the spectra of annulenes. *Michl et al.* [63] [64] proved by site-selected fluorescence and excitation, spectroscopy of bridged [14]annulene in a N_2 matrix that these 'mystery bands' do not correspond to a separate electron transition, but are part of the vibrational structure of the first transition.

It is interesting that *Spanget-Larsen* and *Gleiter* [65] in their study on alkyl-bridged [14]annulenes find that within the CNDO/S-CI model with their parametrization applied, perturbation of the [14]annulene due to twisting, non-planarity, or transannular and hyperconjugative interactions does not bring additional states below the third state (*B* state, *Platt* nomenclature). Our results on [14]annulene are compared in *Table 7* with

Table 7. *Identification of the Theoretical Transitions in the Symmetry Group* C_{2h} *for the Comparison with the 15,16-Dihydro-15,16-dimethylpyrene*

[14]Annulene				15,16-Dihydro-15,16-dimethylpyrene			
Energy [cm^{-1}]	f[a])	Symmetry[b])		Energy [cm^{-1}]	f[a])	Symmetry	
		C_i	C_{2h}			C_{2h}	*Platt*
18546	0.002	A_u	A_u	15164	0.014	A_u	L_b
25523	0.005	A_u	B_u	19681	0.006	B_u	L_a
32308	–	A_g	A_g	25005	–	A_g, B_g	
32677	–	A_g	A_g	26215	–		
34212	–	A_g	B_g	28957	–		
34621	1.038	A_u	A_u	29683	0.530	A_u	B_b
35125	–	A_g	A_g	29844	–	A_g, B_g	
35903	1.572	A_u	B_u	30570	–		
37919	–	A_g	B_g	31861	1.190	B_u	B_a

[a]) f = Oscillator strength.

[b]) Unfortunately, in the C_i symmetry group, all the symmetry-allowed electronic transitions are belonging to the same irreducible representation, namely A_u. To simplify the identification of the transitions, we add *Platt*'s nomenclature.

those of *Spanget-Larsen* and *Gleiter* on *trans*-15,16-dihydro-15,16-dimethylpyrene [65]. Our calculations show that even geometrical changes (as going from the 43- to the 21-configuration) do not lead to the appearance of states which would explain the absorptions at 19000 cm^{-1} as due to an electron transition.

In fact, the position of the $S_1 \leftarrow S_0$, $S_2 \leftarrow S_0$, and $S_3 \leftarrow S_0$ transitions computed for the [14]-21-annulene do not differ appreciably from those computed for the [14]-43-annulene. The main difference is an additional transition for [14]-21-annulene in the region of 40000 cm^{-1}, but since the 21-configuration is present only in 8% relative concentration [12], the probability of observing its transitions is very small.

Conclusions. – As we have earlier postulated [6] [9] [10], [14]annulene (at least the [14]-43-annulene) as [18]annulene is with high probability a cyclic molecule with π-bonds delocalized. Neglect of electron correlation [10] is responsible for the failure of different SCF procedures to reproduce the correct geometry of this type of molecules. According to our computations, the main stabilization of a delocalized structure arises by interaction of the SCF ground state with doubly excited configurations representing promotions of two different occupied to two different virtual orbitals. It was emphasized also that this correlation effect is related to the *Hartree-Fock* instability [66]. *Dewar* and *McKee* [67] recalculated [18]annulene with this aspect of the problem in mind using the MNDO [68] method, but replacing the CI process by the spin-unrestricted *Hartree-Fock* (UHF) approximation [69] [70] which as *Dewar* and *McKee* [67] emphasize 'has been very little used for closed shell systems, presumably because there seems no obvious reason why the electrons in them should be unpaired'. These unpaired electrons perfectly correspond to our above described type of doubly excited configurations! Indeed, the MNDO-UHF structure of [18]annulene shows π-bond delocalization. The present work definitely establishes that [14]-43-annulene has a structure with π-bonds delocalized and further shows that the electron correlation is of crucial importance for the understanding of the UV/VIS spectrum of larger annulenes and related compounds.

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