Structure and energy spectra of molecules containing anti-aromatic ring systems. Part 2. Energy spectra and stabilization of systems containing the anti-aromatic cycloheptatrienide anion †

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The energy spectra and structure of the cycloheptatrienide anion (CHA), annelated CHAs and pyridinium substituted CHAs have been investigated. The band gap of a model polymer with anti-aromatic CHA building blocks is substantially smaller than that of the analogues containing the aromatic cycloheptatrienyl cation.

Molecular π-systems: molecules and polymers with a narrow energy gap (EG) attract widespread scientific and technical interest, *e.g.* as dyes absorbing in the near infrared[1,2] or as 1D-polymers with special electro-physical properties.[3]

In the first communication of this series[4] it was shown that the electronic absorption characteristics of many dye molecules containing five-membered rings with low excitation energies can be explained in terms of the anti-aromaticity of the five-membered ring. It was shown also,[5] that the band structure of a class of quasi-1D-polymers with anti-aromatic structural units are characterized with an EG which is significantly smaller compared with the EG of polymers with aromatic building blocks with an equal number of π-centres in the elementary unit. Earlier investigations[4,5] focussed mainly on π-systems containing anti-aromatic five-membered rings, *i.e.* the cyclopentadienyl cation (CPC). However, CPC is not the only anti-aromatic system attracting interest as a 'building block' ('Baustein', structural principle) of molecular systems with unusual properties. There are other classes of anti-aromatic compounds, quite suitable for the purpose, to which few or no studies have been dedicated, so far. Such is the cycloheptatrienide anion (CHA) **1**, the target of the present study.

The aim of the present work is to extend the theoretical investigations to molecules containing the anti-aromatic CHA.

Compared to the surprisingly large number of longwave absorbing molecules containing CPC as a structural unit,[4,6] little is known about molecules with a CHA as the 'building block'.[7,8] There is at least one reason for this, *viz.* the occupied degenerate HOMOs of CHA are antibonding, which makes the ground state unstable (kinetic instability?). The stability of CHA could be increased by the introduction of electron-accepting substituents,[1] reducing the anti-aromatic character and/or by additional annelation. One of the possible substituents (beside –CN, –NO_2, –CHO, –BH_2), is the pyridinium cation. The model systems studied in the paper are depicted in Fig. 1.

As in the first communication,[4] the following criteria for the anti-aromaticity have been adopted: (*i*) geometry criterion, (*ii*) energy criterion, and (*iii*) charge distribution criterion. The use of these three criteria is discussed in ref. 4.

1D-polymers containing CHA in the elementary unit are interesting as a new class of π-system with translational symmetry and narrow EG. Since the studies of the energy spectrum, which are in progress, require substantially different methods,[5] only one example is given in this paper.

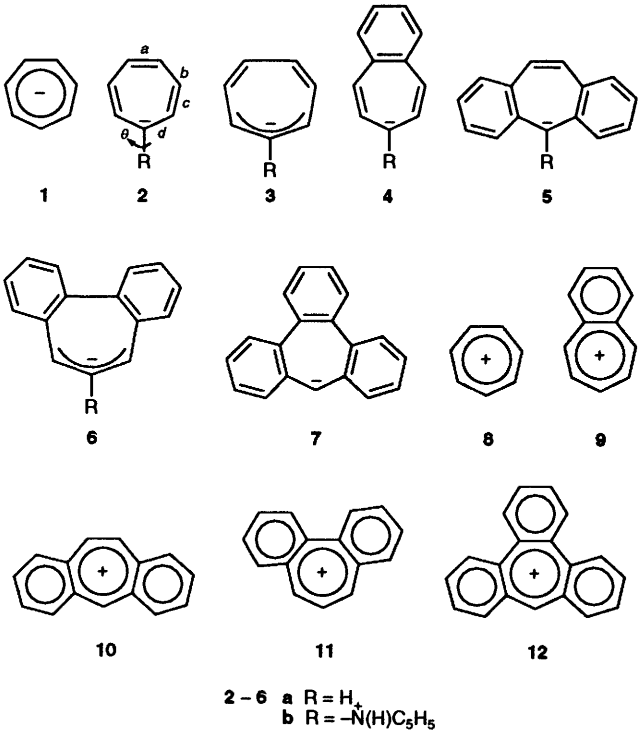

Fig. 1 Structures of the investigated compounds

Computational methods

The results of the investigations have been obtained with different quantum chemical methods. The molecular geometries were optimized using the *ab initio* program system GAMESS-UK[9] with a STO-3G basis set for all the molecules under consideration. The absorption spectral data were calculated based on these geometries using a PPP method.[10,11] The configuration interaction (CI) includes all singly excited (SCI) and double excited (DCI) electron configurations. The experimental value for the longest-wavelength absorption of the CHA could not be reproduced very well by PPP-SCI. As in the case of the CPCs,[4] we have used the PPP-DCI procedure to calculate the energy spectra for this class of compounds (anions). For anions the inclusion of the DCIs is more necessary, because the wave functions of cations are better than those of anions with one and the same basis set.[12]

The dependence of the resonance integrals on the distance *r* is

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† Part 1, ref. 4.

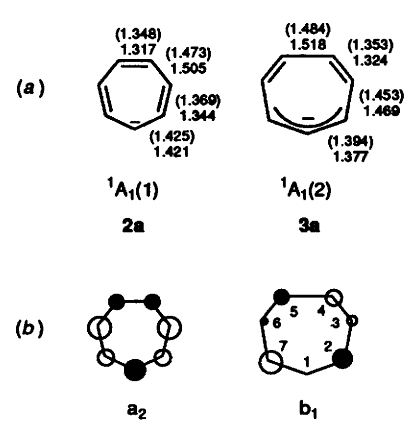

Fig. 2 Molecular geometries (*a*) and HOMO wave functions (*b*) of the equilibrium Jahn–Teller forms of the CHA. The bond lengths were optimized by an *ab initio* procedure (STO-3G basis set); in brackets are given the results of Zwaard *et al.*[7] using the semiempirical MINDO/3 method. The wave functions were obtained with the HMO method. The HOMO (π_4) of the $^1A_1(1)$ Jahn–Teller form belongs to the a_2 irreducible representation and the HOMO of the $^1A_1(2)$ form to the b_1 representation.

Table 1 Bond lengths (in Å): $r_a - r_d$ (see Fig. 1) within the CHA ring and r_e of the bond between the CHA and the pyridinium substituent of the equilibrium Jahn–Teller forms[a]

Compd.	r_a	r_b	r_c	r_d	r_e
2a	1.317	1.505	1.344	1.421	—
3a	1.518	1.324	1.469	1.377	—
4a	1.449	1.488	1.351	1.406	—
5a	1.318	1.495	1.434	1.415	—
6a	1.557	1.444	1.443	1.369	—
7	1.444	1.538	1.434	1.403	—
2b	1.321	1.479	1.329	1.474	1.379
4b	1.408	1.487	1.328	1.464	1.387
5b	1.299	1.471	1.450	1.581	1.480

[a] The results have been obtained with the *ab initio* method (GAMESS-UK,[9] STO-3G basis set).

considered using Mulliken's formula:[13] $\beta(r) = \beta_0 S/S_0$ [S is the overlap integral, $\beta_0 = -2.79$ eV, the optimized resonance integral for DCI calculations for the C–C bond at 1.4 Å (ref. 14)]. The two-electron Coulomb integrals $\gamma_{\mu\nu}$ were calculated with the Mataga–Nishimoto approximation.[15]

Special parameters for the nitrogen atom, optimized for PPP-DCI calculations of cyanines,[14] were used: $\Delta I_N = -16.78$ eV, $\gamma_{NN} = 15.92$ eV, $\beta_{CN} = -3.21$ eV ($r = 1.4$ Å).

Results and discussion

Geometry criterion

The typical anti-aromatic monocyclic molecules with $4n\pi$-electrons in cyclic conjugation and D_{mh} symmetry ($m = 3, 5, 7, \ldots$) are Jahn–Teller active systems.[16,17] In this context, the CHA was first investigated by Zwaard *et al.*[7] by means of the semiempirical MINDO/3 method. In Fig. 2 are presented the results of the *ab initio* geometry optimization. They are in line with Zwaard's results[7] (the values in brackets). Nonetheless, the geometry of the seven-membered ring in the derivatives corresponds to one of the two stable Jahn–Teller forms: $^1A_1(1)$ or $^1A_1(2)$. This can be seen in Table 1, where the *ab initio* optimized geometry parameters of the models under study are collected. Similarly to the CPC derivatives,[4] the geometry of the CHA derivatives features drastic bond alternation.

The analogy in the geometry of the Jahn–Teller forms of CHA [$^1A_1(1)$ and $^1A_1(2)$] and its derivatives is not accidental. Qualitatively, this can be illustrated with the mono-substituted CHA.

In Fig. 2 are also presented the coefficients c_r of the HOMO belonging to the b_1 irreducible representation (IR) for the $^1A_1(2)$ form, respectively, to the a_2 IR for the $^1A_1(1)$ form. The radii of the circles are proportional to the values of the coefficients $|c_r|$ [$c_r > 0$ (●), $c_r < 0$ (○)]. The numerical values are obtained by means of the HMO method for the geometry of the two Jahn–Teller forms shown above (the values of c_r for the degenerate e'_1 MOs of CHA do not differ substantially from those in Fig. 2).

When the HOMO belongs to the b_1 IR, the bond orders correspond to the $^1A_1(2)$ structure [c(●)c(●) > 0, c(●)c(○) < 0, c(○)c(●) < 0]. For example, the C_4–C_5 bond order of the $^1A_1(2)$ form decreases by $c_4{}^2$ (HOMO). When the HOMO belongs to the a_2 IR, the bond orders correspond to the $^1A_1(1)$ structure, and the C_4–C_5 bond order increases with $c_4{}^2$ (see Fig. 2).

Qualitatively, the coefficients of the HOMO with b_1 symmetry in the seven-membered ring of CHA derivatives are the same as those of the $^1A_1(2)$ form; likewise, the coefficients of the HOMO with a_2 symmetry in the seven-membered ring of CHA derivatives correspond to the ones of the $^1A_1(1)$ form. This is the reason for the parallel behaviour in the bond orders, respectively, of the geometry of the forms with identical HOMO symmetry.

The above qualitative result (in the π-electron approximation) follows directly from the LCMO representation.[18]

The degenerate π-MOs in CHA [Fig. 3(*b*)] belong to the two-dimensional representation e'_1. When the symmetry of the cycle is reduced (from D_{7h} to C_{2v}), due to the Jahn–Teller distortion, the wave functions corresponding to these e'_1 representations are transformed to functions belonging to the irreducible representations b_1 and a_2 (see Fig. 2).

$$\Psi_k(a_2) = c_{k1}\varphi_1 + c_{k2}(\varphi_2 + \varphi_7) + c_{k3}(\varphi_3 + \varphi_6) + c_{k4}(\varphi_4 + \varphi_5) \quad (1a)$$

$$\Psi_k(b_1) = c_{k2}(\varphi_2 - \varphi_7) + c_{k3}(\varphi_3 - \varphi_6) + c_{k4}(\varphi_4 - \varphi_5) \quad (1b)$$

On substitution of a hydrogen atom in the $^1A_1(1)$ or $^1A_1(2)$ Jahn–Teller form with a heteroatom or a many-atom fragment R, having C_{2v} symmetry (or having a C_2 axis coinciding with the C_2 axis of the starting form), the MOs of the substituted system also belong to the a_2 or b_1 IR.

Let us denote by [$\chi_p(b_1)$] and [$\chi_q(a_2)$] the MOs of the substituent R [when the substituent is an atom, $\chi(a_2) = \varphi - 2p_Z$AO].

Since the matrix elements $\Psi_k(b_1)|H|\chi_p(b_1) = 0$ and $\Psi_k(b_1)|H|\chi_q(a_2) = 0$, the MOs of CHA and the substituent belonging to the b_1 IR are left unchanged. Only the energies of the MOs belonging to the a_2 IR are affected. In the LCMO representation they are given by eqn. (2).

$$\Phi p(a_2) = \sum_k c_{rk}\Psi_k(a_2) + \sum_q c_{rq}\chi_q(a_2) \quad (2)$$

For the substituent under consideration—the pyridinium cation—the relative position of the HOMO with b_1 or a_2 symmetry is preserved for the derivatives of both the $^1A_1(1)$ and the $^1A_1(2)$ forms.

Energy criterion

Anomalously low values of the excitation energies (ΔE) and a blue shift of the longwave transition on perturbation

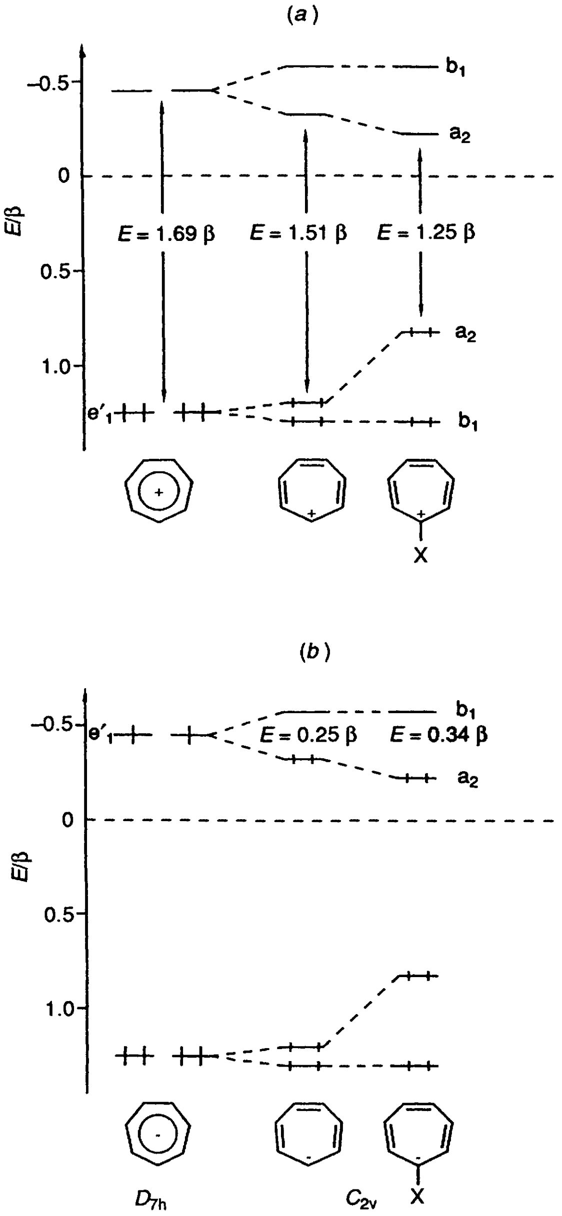

Fig. 3 Change of the HOMO–LUMO energy difference, ΔE, resulting from a perturbation by increasing the conjugated π-electron system in the case of the aromatic CHC (*a*) and the anti-aromatic CHA (*b*)

Table 2 Calculated excitation energies (ΔE/eV) and sums of the π-net charges of the CHA fragment (Q_7) of the CHA, its annelated compounds and of pyridinium-substituted CHAs. The experimental (ΔE_{exp}/eV) and calculated (ΔE_{calc}/eV) excitation energies for the respective CHCs are quoted for comparison

Compd.	ΔE	Q_7	Compd.	ΔE_{exp}[a]	ΔE_{calc}
2a	1.24	−1.000	**8**	4.52	4.51[b]
3a	1.22	−1.000			
4a	2.02	−0.676	**9**	2.92	3.03[c]
5a	2.81	−0.403	**10**	2.30	2.75[c]
6a	2.80	−0.494	**11**	2.71	2.87[c]
7	2.87	−0.451	**12**	2.21	2.44[b]
2b	3.93	−0.647			
4b	4.04	−0.627			
5b	3.81	−0.534			

[a] Ref. 21. [b] Ref. 22. [c] Ref. 23.

Table 3 Dependence of the excitation energy (ΔE/eV) of the total π-electron energy (E^{π}/eV) and of the sum of the π-net charges within the seven-membered ring (Q_7) on the torsional angle θ (in degrees) between CHA and the pyridinium group of **2b**

θ	ΔE	E^{π}	Q_7
0	3.93	−192.49	−0.647
30	3.78	−191.98	−0.692
45	3.57	−191.42	−0.754
60	3.32	−190.81	−0.840
90	2.97	−190.06	−1.000

(extension) of the conjugated 4*n*π-electron system are typical features of anti-aromatic compounds.[4]

Contrary to this, a perturbation of the conjugated system of aromatic monocyclic compounds with $(4n + 2)$π-electrons, caused by the substitution of a hydrogen atom by a π-electron fragment X or by annelation, results in a decrease of the energetic distance between the HOMO and the LUMO [$\Delta E = E(\text{LUMO}) - E(\text{HOMO})$] and, therefore, in a red shift. The different behaviour of the spectroscopic shift of aromatic $(4n + 2)$π-systems and of anti-aromatic 4*n*π-systems is demonstrated in Fig. 3 in the case of the cycloheptatrienyl cation (CHC) and the CHA.

The experimental value for the CHA is $\Delta E = 1.65$ eV (750 nm),[19] whereas for the heptaphenyl substituted CHA $\Delta E = 2.20$ eV (563 nm).[20] The extension of the π-electron system of the CHA by seven phenyl groups is connected with a significant blue shift of about 200 nm of the longest-wavelength absorption.

The excitation energies for the longest-wavelength absorption for the CHA, CHC and their annelated derivatives (see Fig. 1) are collected in Table 2. In the case of the aromatic CHC and the annelated CHCs a red shift of the experimental[21] and calculated (HMO-SCI,[22] PPP-SCI[23]) values can be observed. Contrary to this, the anti-aromatic CHAs show growing excitation energies with increase of annelation (**2a**, **3a**→**4a**→**5a**, **6a**→**7**).

Substitution of a hydrogen atom in CHA and the annelated CHAs by a positively charged pyridinium group should stabilize these systems and, at the same time, reduce their anti-aromatic character. By such a substitution the conjugated π-electron system is extended, which is connected with a blue shift relative to the unsubstituted compounds. This can be seen from the comparison of the ΔE data for the unsubstituted and the pyridinium substituted CHAs and the annelated CHAs given in Table 2. In Table 2 are collected the data only of those pyridinium substituted CHAs in which the CHA corresponds to the $^1A_1(1)$ Jahn–Teller form: **2b**, **4b** and **5b**. The pyridinium substituted CHAs **3b** and **6b** correspond to the $^1A_1(2)$ Jahn–Teller form of the CHA. These are much less stable in relation to the corresponding isomers **2b** and **5b**, respectively.

The pyridinium substituted dibenzo[*b*,*f*]CHA **5b** shows a lower excitation energy than the pyridinium substituted monobenzoCHA **4b** and pyridinium substituted CHA **2b**. The reason for this behaviour of **5b** is an overcompensation of the anti-aromatic character of the CHA fragment by the two aromatic benzene rings condensed with the CHA and by the heteroaromatic pyridinium substituent.

A further argument for the anti-aromatic character of the CHA can be drawn from the influence on the excitation energy of the perturbation of the conjugated π-system of pyridinium substituted CHA **2b** by torsion of the pyridinium group.

The corresponding ΔE data together with the sum of the π-electron net charges of the seven-membered ring Q_7 and the total π-electron energy E^{π} of **2b** are given in Table 3. The greater the torsional angle θ, the smaller the conjugation between the

CHA and the pyridinium group and the smaller the excitation energy, *i.e.*, the extension of conjugation is connected with a blue shift. The total π-electron energy decreases in the same direction. The dependence of the resonance integral β_{CN} between the CHA and the pyridinium substituent on the torsional angle θ was taken into account using the equation $\beta_{CN} = \beta^{\circ}_{CN} \cos\theta$ [$\beta^{\circ}_{CN} = -3.21$ eV (ref. 14)].

Charge distribution criterion

The sum of the π-net charges within the seven-membered ring of the CHA (Q_7) is given by eqn. (3) (Z_μ is the core change of the atom μ).

$$Q_7 = \sum_{\mu}^{7} (Z_\mu - q_\mu) = \sum_{\mu}^{7} (1 - q_\mu) = -1 \qquad (3)$$

The substitution of a hydrogen atom by a pyridinium group and/or annelation of CHA decreases Q_7 (see Table 2). A torsion of the pyridinium substituent has the same effect: the greater the perturbation of the π-system of CHA (*i.e.*, the smaller the torsional angle θ and, therefore, the greater the conjugation between the CHA and the pyridinium group), the smaller is Q_7 (see Table 3).

There is a qualitative correlation between the excitation energy (ΔE) and the sum of the π-net charges Q_7: the greater Q_7, the smaller the excitation energy ΔE. An exception is the pyridinium substituted dibenzoCHA **5b**, for which a red shift was obtained with respect to the monobenzo and non-fused pyridinium substituted CHAs **2b** and **4b** due to the over-compensation of the anti-aromatic character of the CHA by the two benzene rings and the pyridinium substituent.

Therefore, the sum of π-net charges within the seven-membered ring of CHAs, Q_7, can be used as an additional qualitative criterion for recognition of the anti-aromatic character of molecules with a CHA fragment.

Energy spectra of 1D-polymers containing CHA in the elementary unit

In an earlier paper[5] it was shown that the energy gap of polymers containing the anti-aromatic cyclopentadienyl cation in the elementary unit (EU) is significantly smaller compared with the EG of polymers with aromatic cyclopentadienide anions as building blocks in the EU. As shown in ref. 5, two opposite effects influence the energy spectrum on coupling of anti-aromatic structures in a 1D-polymer in one-electron approximation: (*i*) the perturbation of the anti-aromatic building blocks results in a splitting of the degenerate frontier MOs (see Fig. 3) increasing the HOMO–LUMO gap; (*ii*) the formation of bands by the splitting of the frontier MOs is connected with a decrease of the HOMO–LUMO band gap of the polymer.

Taking into account the electron correlation may change the band gap obtained with the one-electron approximation, an exact prediction of the band gap width without estimation of the electron correlation is impossible.

In order to illustrate the difference in the EG width for the two classes of polymers: aromatic and anti-aromatic, only one example of a polymer with its aromatic (PAR) and anti-aromatic (PAN) forms is given (see Fig. 4).

The results from the investigations of the above polymers, as well as the band structure of a large class of anti-aromatic polymers, containing CHA in the elementary unit (EU), will be published later.

The energy spectra of the polymers are calculated within a formalism described earlier.[5,24–27] It was shown,[27] that the energy gap of a regular π-system in its singlet ground state can be expressed by the formula (4), where Δ_{top} and Δ_{geom} are factors depending on the molecular topology and geometry, respectively. $\Delta_{1,corr}$ and $\Delta_{2,corr}$ are correlation corrections.

$$\Delta E = \sqrt{\Delta_{1,corr}{}^2 + (\Delta_{2,corr} + \Delta_{top} + \Delta_{geom})^2} \qquad (4)$$

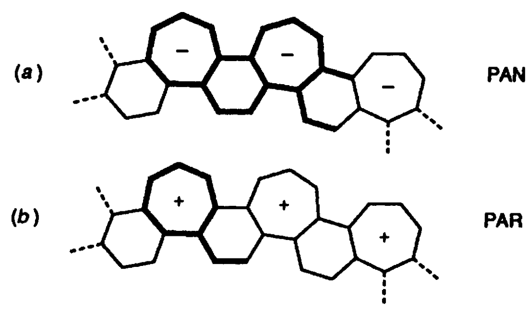

Fig. 4 Polymer models with anti-aromatic CHA (PAN) (*a*) and aromatic CHC (PAR) (*b*) building block in the elementary unit. The EUs are designed with bold lines.

Table 4 Components to the energy gap Δ_{top}, Δ_{geom}

Polymer	Δ_{top}/eV	$\Delta_{geom} + \Delta_{top}$/eV	ΔE^a/eV
PAN	1.70	1.75	0.72
PAR	0.0	0.08	1.97

[a] The energy gap ΔE of the investigated polymers was calculated according to eqn. (4a).

The polymers are assumed to be planar 1D regular systems with periodic boundary conditions. The topological and geometrical components to the EG are calculated in the tight-binding approximation—a Hückel–Hubbard version of the Bloch method.[27] The topological component, Δ_{top}, was calculated with ideal geometry; all bond lengths and resonance integrals are equal ($r = r_0 = 1.4$ Å, $\beta = \beta_0 = -2.4$ eV). For the estimation of the geometrical component, Δ_{geom} (Peierls' distortion) a generalized Su–Schrieffer–Heeger (SSH) model,[28] described in ref. 29 is used. The dependence of the resonance integrals on the bond lengths is determined by the Mulliken formula.[13]

The application of the generalized SSH method yields bond length alternation for both PAR and PAN. However, the results for the two polymer forms are qualitatively different. In the case of PAN the bond alternation, reflecting the electron–phonon interaction, leads to doubling of the EU, whereas for PAR this does not occur.

The correlation correction terms $\Delta_{1,corr}$ and $\Delta_{2,corr}$ were calculated with a formalism, described in ref. 27, using a standard value for the one-centre Coulomb integral of the carbon atom (Hubbard parameter), $\gamma_{CC} = 5.4$ eV.[5,24,25]

In Table 4 are collected the calculated values of the EG and its components for the anti-aromatic PAN and aromatic PAR polymers.

The energy gap of the polymer with anti-aromatic character, PAN, is substantially smaller than that of the polymer with aromatic structural units, PAR. While the geometrical contributions to the EG, Δ_{geom}, are comparable for both polymers, the topological components, Δ_{top}, differ significantly.

Conclusions

CHA and their annelated and pyridinium substituted derivatives show the typical features of anti-aromatic compounds. Therefore, these molecular systems, besides the anti-aromatic CPCs,[4,5,6] can be building blocks for new materials with specific properties.

Acknowledgements

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References

1 J. Fabian and R. Zahradnik, *Angew. Chem.*, 1989, **101**, 693.
2 J. Fabian, H. Nakazumi and M. Matsuoka, *Chem. Rev.*, 1992, **92**, 1197.
3 Ed. H. Kies, *Conjugated Conducting Polymers*, Springer Series in Solid-state Sciences, vol. 102, Springer Verlag, Berlin, 1992.
4 Part 1, F. Dietz, N. Tyutyulkov and M. Rabinovitz, *J. Chem. Soc., Perkin Trans. 2*, 1993, 157.
5 F. Dietz, K. Müllen, M. Baumgarten and N. Tyutyulkov, *Makromol. Chem., Theor. Simul.*, 1994, **3**, 241.
6 R. Gompper and H.-U. Wagner, *Angew. Chem.*, 1988, **100**, 1493.
7 A. W. Zwaard, A. M. Brouwer and J. J. C. Mulder, *Recl. Trav. Chim. Pays-Bas*, 1982, **101**, 137.
8 M. N. Gluhovtzev, B. Ja. Simkin and M. J. Minkin, *Usp. Khim.*, 1985, **54**, 86.
9 GAMESS-UK; Computational Science Group, Daresbury Laboratory, UK.
10 R. Pariser and R. Parr, *J. Chem. Phys.*, 1953, **21**, 466; 767.
11 J. Pople, *Trans. Faraday Soc.*, 1953, **49**, 1375.
12 A. C. Hopkinson, in *Progress in Theoretical Chemistry*, ed. I. G. Csizmadia, vol. 2, Elsevier, Amsterdam, Oxford, New York, 1977, p. 194.
13 R. Mulliken, *J. Chem. Phys.*, 1949, **46**, 497; 675.
14 F. Dietz, J. Fabian, G. Olbrich, N. Tyutyulkov and I. Kanev, *Commun. Dept. Chem. Bulg. Acad. Sci.*, 1982, **15**, 519.
15 N. Mataga and K. Nishimoto, *Z. Phys. Chem., Frankfurt*, 1957, **13**, 140.
16 A. D. Lieher, *J. Phys. Chem.*, 1963, **67**, 389.
17 W. T. Borden, *Diradicals*, Wiley, New York, 1982.
18 M. J. S. Dewar, *The MO Theory of Organic Chemistry*, McGraw-Hill, New York, 1969.
19 H. J. Dauben and M. R. Rifi, *J. Am. Chem. Soc.*, 1963, **85**, 3041.
20 R. Breslow and H. W. Chang, *J. Am. Chem. Soc.*, 1962, **84**, 1484; 1965, **87**, 2200.
21 G. Naville, H. Strauss and E. Heilbronner, *Helv. Chim. Acta*, 1960, **43**, 1221.
22 J. Koutecky, P. Hochmann and J. Michl, *J. Chem. Phys.*, 1964, **40**, 2439.
23 N. Tyutyulkov, F. Fratev and M. Ivanova, *Theor. Chim. Acta*, 1971, **20**, 385.
24 M. Baumgarten, S. Karabunarliev, K.-H. Koch, K. Müllen and N. Tyutyulkov, *Synth. Met.*, 1992, **47**, 21.
25 N. Tyutyulkov, S. Karabunarliev, K. Müllen and M. Baumgarten, *Synth. Met.*, 1993, **53**, 205.
26 O. E. Polansky and N. Tyutyulkov, MATCH, 1977, **3**, 149.
27 N. Tyutyulkov and F. Dietz, *Chem. Phys.*, 1993, **171**, 293.
28 W.-P. Su, J. R. Schrieffer and A. J. Heeger, *Phys. Rev. Lett.*, 1979, **42**, 1698; *Phys. Rev. B*, 1980, **22**, 2099.
29 S. Karabunarliev, M. Baumgarten, K. Müllen and N. Tyutyulkov, *Chem. Phys.*, 1994, **179**, 421.

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