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The electronic structures of some extended conjugated electron acceptors within the Hartree–Fock approximation and beyond the mean-field approach as verified by the Hartree–Fock instabilities

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The electronic structures of the extended conjugated electron acceptors **1**–**3** were investigated within the framework of a semiempirical INDO and a π-electronic Hartree–Fock Hamiltonian. Utilizing Koopmans' theorem, predictions are made of the magnitude of the ionization potentials and the electron affinities and their dependence on the molecular geometry ("olefinic" vs. "aromatic") and the nature of the acceptor functions. The validity of the Hartree–Fock approximation has been studied by means of the Thouless stability conditions. The INDO and π-SCF wave functions turn out to be adequate descriptions of the ground states of **1**–**3**. A single particle hole pair, due to a small energy separation between the highest occupied and lowest virtual orbital and a large Coulomb integral with respect to these orbitals leads to non-singlet (triplet) instabilities or near instabilities of the wave functions indicating the importance of spin correlation in **1**–**3**.

Key words: Extended conjugated electron acceptors—electronic structure in the INDO and π-electronic approximations—Hartree–Fock instabilities

1. Introduction

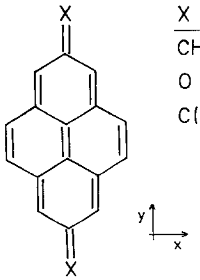
The synthesis of the tetrathiafulvalene (TTF)/7,7,8,8-tetracyanoquinodimethane (TCNQ) complex and the discovery of its remarkable conductive properties caused an intense search for further "organic metals" or even for organic high-temperature super conducting compounds [1]. The quest for new derivatives of

TTF or related donors turns out more fruitful than that for new acceptors superior to TCNQ where one thinks mainly of TCNQ analoga with more extended conjugated π-systems [2]. Such acceptors should exhibit smaller on-site electron-electron repulsion which is important for the conductive properties in the simple framework of the Hubbard Hamiltonian [1, 3]. Furthermore the use of donors larger than TTF requires acceptors larger than TCNQ, since the organic metal donors and acceptors should be of comparable size [4]. Moreover extended acceptors might be of interest as building blocks in cyclophanes where the interaction with a strong donor could lead to a biradical-ionic ground state [5].

The synthesis of extended TCNQ analoga is certainly not an easy task and one of the few hitherto known examples is 13,13,14,14-tetracyanopyreno-2,7-quinodimethane (TCNP) **3** [6, 7] (cf. Fig. 1). However, not much is known experimentally about the acceptor capability of **3** and therefore a theoretical investigation of such extended acceptors is desirable on condition that the utilized theoretical procedures allow reliable conclusions on the electronic structure and the molecular observables of interest, e.g. electron affinities EA.

Usually the independent particle model in the form of the restricted Hartree–Fock (HF) approximation with its mean-field approach serves as a starting-point for most of the quantum chemical calculations, both of the *ab initio* and the semiempirical type. Even procedures beyond HF, e.g. configuration interaction schemes, proceed generally from HF orbitals for the ground state. The stability of the independent particle approach and the importance of many-body effects can be studied by means of the Thouless stability conditions [8] or their extensions with respect to the electronic structure of molecules by Čižek and Paldus [9].

Our studies on the HF instabilities of the TTF/TCNQ system [10] have shown that TCNQ represents a (nearly) HF unstable (non-singlet, see next chapter) molecule where above all spin correlation is important. It is an interesting theoretical question whether HF instabilities will be more likely with larger TCNQ analoga or similar compounds. Consequently in the present publication we want to investigate the conjugated planar systems **1–3** displayed in Fig. 1 with respect to the electronic structure, some molecular observables like the EA or the ionization potential IP, and the HF stability conditions. We expect an elucidation of the following questions: (i) How do the electronic structure and the molecular



X	
CH_2	1
O	2
$C(CN)_2$	3

Fig. 1. Compounds under study

observables of interest depend on the nature of the electron withdrawing group X, i.e. what kind of changes are induced by the replacement of $X=CH_2$ (**1**) by $X=O$ (**2**) and $X=C(CN)_2$ (**3**)? (ii) How do geometrical parameters influence the electronic structure? (iii) Does the HF approach represent an adequate description of the ground state of **1–3**?

2. Computations method

Ab initio procedures are prohibitive due to the size of the molecules of interest. Therefore we use a recently developed semiempirical INDO Hamiltonian [11] being parametrized in order to mimic the computational results of time consuming high quality *ab initio* methods in the framework of dressed renormalized two-electron integrals leading to a reduction of the residual interaction. In order to study the dependence of the electronic structure on the geometry of the compounds **1–3** we have chosen two geometrical models. In the "olefinic" model (denoted as **1a**, **2a** and **3a**) we use alternating bond lengths corresponding to the formulae given in Fig. 1, whereas a common aromatic bond length is taken for all CC bonds in the pyrene unit in the "aromatic" model (denoted as **1b**, **2b** and **3b**). Standard values [12] have been taken for all bond lengths.

Since **1–3** are planar conjugated systems we shall compare the results of the INDO Hamiltonian with those of the π-electronic approach which was used extensively in HF and instability calculations on extended π-systems [13]. The π-SCF procedure employed here is that of Younkin et al. [14] which was successfully applied to the calculation of EAs and IPs and excited states of negative ions of a large series of conjugated compounds. This π-SCF method yields automatically self-consistent bond lengths which do not depend on the starting geometry, i.e. the olefinic or the aromatic geometrical model.

The stability conditions for the restricted HF wave function Ψ_0 are given by the eigenvalue problems

$$M^a C^a = \lambda^a C^a \tag{1}$$

where $a=s$, c or t stands for the singlet, non-real (complex) or non-singlet (triplet) instability problem [9, 15, 16]. The matrix elements of M^a are given as follows

$$M^a_{ik,ik} = \varepsilon_k - \varepsilon_i + f_a K_{ik} - J_{ik} \tag{2}$$

$$M^a_{ik,jl} = g_a(ik|jl) + h_a(il|jk) - (ij|kl) \tag{3}$$

where $(f_a, g_a, h_a) = (3, 4, -1)$ if $a=s$, $(1, 0, 1)$ if $a=c$ and $(-1, 0, -1)$ if $a=t$. The indices ik/jl symbolize orbital fluctuations (OFs) $\phi_i \rightarrow \phi_k / \phi_j \rightarrow \phi_l$ from the occupied HF orbitals ϕ_i, ϕ_j into the virtual ones ϕ_k, ϕ_l. J_{ik} and K_{ik} are the Coulomb and exchange integrals of the orbitals ϕ_i and ϕ_k and the four-index integral $(ij|kl)$ is defined by $\langle \phi_i(1)\phi_j(1)|e^2 r_{12}^{-1}|\phi_k(2)\phi_l(2)\rangle$.

The global stability condition (singlet, complex and triplet) of the HF wave function Ψ_0 requires that all eigenvalues λ^a are positive, Ψ_0 is called singlet unstable if at least one $\lambda^s \leq 0$. Then there exists another closed shell wave function Ψ which is degenerate with Ψ_0 ($\lambda^s = 0$) or lower in energy ($\lambda^s < 0$). The spatial symmetry is broken in Ψ if the associated eigenfunction C^s consists of OFs $\phi_i \rightarrow \phi_k$ where ϕ_i and ϕ_k belong to different irreducible representations of the spatial point group of the molecule. Such solutions are usually called charge density waves [16]. In the case of a $\lambda^t \leq 0$ Ψ_0 is called non-singlet (triplet) unstable and an unrestricted HF solution (spin-density wave [17]) exists with the same or lower energy than that of Ψ_0. A vanishing or negative λ^c indicates the existence of a complex set of one-electron wave functions with equal or lower energy and Ψ_0 is called non-real (complex) unstable. As in the case of singlet instability the spatial symmetry may be violated in the unrestricted or complex solution if the OFs $\phi_i \rightarrow \phi_k$ described by C^t or C^c do not transform according to the totally symmetric representation of the spatial point group.

The study of the Thouless instability conditions is a successful approach to analyze the importance of electron correlation *and* possible symmetry violations in the molecular systems. Electron correlation alone could also be investigated by means of an ordinary configuration interaction scheme. However, the huge number of doubly excited configurations leads to considerably larger matrices than M^a, since M^a is made up only from single excitations.

In the case of **1–3** (INDO) or **3** (π-SCF) the eigenvalue problems (1) had to be restricted to 121 (INDO) and 100 (π-SCF) OFs due to our current computational capacities. The neglected OFs would slightly reduce the lowest λ^a roots. Therefore the criterion $\lambda^a \leq 0$ for defining unstable HF solutions is replaced by the approximate criterion $\lambda^a \leq \eta$ where η is a small positive energy. Semiempirical Hamiltonians with dressed two-electron integrals, as for example the Hamiltonians used here, implicitly contain part of the correlation effects and of the screening of the core electrons [18]. Consequently λ^a values obtained in the framework of *ab initio* methods will be significantly lower although the nature of the corresponding eigenfunctions C^a and the constituent OFs will be the same [19].

The starting orbitals for the HF procedure are obtained by a Hückel-type approach. The SCF-iterations are performed with preselected configurations and Hartree-damping [20] is employed in the case of the INDO calculations.

3. The electronic structures of 1–3 on the HF level

Compound **1** belongs to the class of alternant hydrocarbons. Consequently the π-SCF procedure with the tight-binding approximation for the resonance integrals produces a uniform charge distribution. This is approximately verified by our INDO calculation where the small deviations from the uniform charge distribution are mainly caused by the polarity of the C—H bonds. The heteroatoms in **2** and **3** do not lead to significant changes in the INDO charges in the pyrene unit with respect to **1**, only the C=O bonds in **2** and, to a lesser extent, the C≡N bonds in **3** are polarized as expected. Differences in the charge distributions of the olefinic and the aromatic geometrical model are negligible. Without an additional

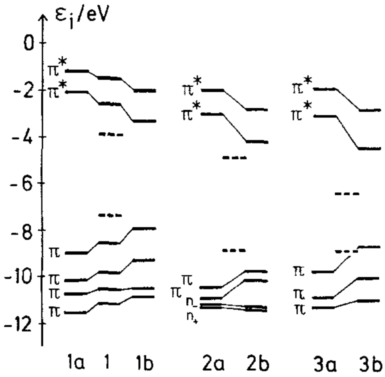


Fig. 2. Orbital energy scheme for 1–3 according to the INDO (——) and π-SCF method (---)

geometry optimization which would be too computer time intensive we cannot definitively conclude from our INDO results on the energetical most favorable geometry of **1–3**. The self-consistent bond lengths of the π-SCF procedure in the pyrene unit of **1–3** are intermediate with respect to the olefinic (**Xa**) and aromatic (**Xb**) models.

According to Koopmans' theorem [21] the orbital energies ε_h and ε_l of the highest occupied orbital (HOMO) ϕ_h and the lowest virtual orbital (LUMO) ϕ_l are measures for IP and EA, i.e. $IP \cong -\varepsilon_h$ and $EA \cong -\varepsilon_l$. The INDO orbital energy scheme is displayed in Fig. 2. We can assume that the olefinic and aromatic models constitute the upper and lower limits of ε_h and ε_l. This is verified in the case of **1** where we have repeated the INDO calculations utilizing the π-SCF bond lengths. IPs obtained with Koopmans' theorem from the INDO ε_h values are generally too high by about 1 eV [11]. Taking this into account we obtain for **1**, **2** and **3** IPs in the range 6.9-8.0, 8.7–9.5 and 7.7–8.8 eV where the smaller values are connected with the aromatic geometries **Xb**. So far there is not much experience about the correlation of EA and ε_l, but the comparison of the calculated $\varepsilon_l = -3.0$ eV [10] and the experimental $EA = 2.8$ eV [22] for TCNQ suggests that EAs calculated by means of Koopmans' theorem are too large by about 0.2 eV. With such a correction we predict for **1**, **2** and **3** EAs in the range 1.9–3.1, 2.8–3.9 and 2.8–4.3 eV, where now the smaller values belong to the olefinic models **Xa**. Obviously larger (smaller) EAs for the aromatic (olefinic) structures correspond to smaller (larger) IPs. As expected EA of **2** is considerably larger than EA of **1** if we compare corresponding geometrical models, i.e. **1a** with **2a** and **1b** with **2b**. However, the difference in ε_l and hence in EA between **2** and **3** is smaller than that between **1** and **2**. The π-SCF LUMO energies ε_l decrease in the series **1–3**, cf. Fig. 2. According to the regression line (12) in Ref. [14] we obtain EAs for **1**, **2** and **3** of 1.8, 2.7 and 4.1 eV. Thus both theoretical methods predict an increase of the acceptor capability in the series **1–3**. The TCNQ analogue **3** should be a significantly better electron acceptor than TCNQ with $EA_{exp} = 2.8$ eV [22]. Similar as with the INDO approach the π-SCF model predicts an increase of IP from **1** to **2**, whereas the ratio of the IPs of **2** and **3** is different with both numerical procedures. By using the regression line (13) of Ref. [14] the π-SCF Hamiltonian predicts IPs for **1** and **2** or **3** of 6.4 and 7.9 eV.

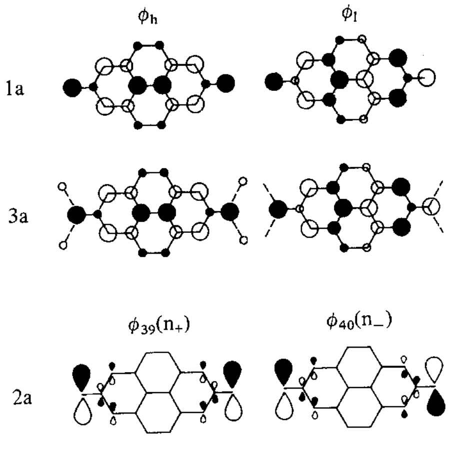


Fig. 3. Schematical representation of the INDO frontier π-orbitals of **1a** and **3a** and of the non-bonding orbitals ϕ_{39} (n_+) and ϕ_{40} (n_-) of **2a**

The decrease of ε_h and ε_l caused by the replacement of the acceptor function $X{=}CH_2$ in **1** by $X{=}O$ in **2** can easily be rationalized by using first order perturbation theory since firstly the π-orbitals ϕ_h and ϕ_l are related through the approximate validity of the pairing theorem [23] and secondly the orbital coefficients on the acceptor functions X are numerically large, cf. Fig. 3 where HOMO and LUMO of **1a** and **3a** are displayed as representative examples. The corresponding orbitals of **2a** or the aromatic models and of the π-SCF procedure for **1**–**3** are similar to those given in Fig. 3. Such simple arguments are inapplicable for the comparison of **2** and **3**. Only the analogy with *p*-benzoquinone and TCNQ with $EA_{exp} = 1.8$ and 2.8 eV [22] suggests that **3** should be a considerably better acceptor than **2**. Another consequence of the approximate validity of the pairing properties of HOMO and LUMO of **1**–**3** within the INDO approach is the smaller HOMO-LUMO gap $g = \varepsilon_l - \varepsilon_h$ for the aromatic models **Xb** with respect to the corresponding olefinic ones **Xa**, cf. Fig. 2. According to first order perturbation theory the lengthening of the formal double bonds in **Xa** increases ε_h but decreases ε_l due to the phases of the π-basis functions in HOMO and LUMO, cf. Fig. 3. On the other hand the shortening of the formal single bonds in **Xa** reduces ε_h as well as ε_l. Therefore the LUMO is necessarily stabilized whereas the destabilizing effects obviously preponderate in the HOMO.

4. HF instabilities of the INDO HF wave functions

The INDO calculations lead to a decreasing HOMO-LUMO gap g in the order $\mathbf{2} > \mathbf{1} > \mathbf{3}$, cf. Table 1. A small HOMO-LUMO gap g is a first hint at the possible inadequacy of the HF one-determinant solution for the ground state. The aromatic geometries **Xb** exhibit g values which are smaller by at least 1.8 eV than those of the corresponding olefinic structures **Xa** and even smaller than that calculated for the TTF/TCNQ system [10] which is characterized by non-singlet instabilities. Therefore the occurrence of HF instabilities should be considered in electronic structure investigations of **1**–**3**.

All studied compounds are singlet stable, i.e. $\lambda_1^s \gg 0$. Consequently no other wave functions exist with closed shell character and with real orbitals which have similar or lower energy than the HF wave function Ψ_0. The eigenfunctions C_1^s associated with λ_1^s describe OFs of the $\pi \rightarrow \pi^*$ excitation type. Only in the case of **2a** these OFs are connected with λ_3^s whereas the slightly smaller $\lambda_{1,2}^s$ belong to eigenfunctions $C_{1,2}^s$ consisting of OFs of the $n \rightarrow \pi^*$ type. The eigenfunctions with $\pi \rightarrow \pi^*$ nature C_1^s of **1a**/**b**, **2b** and **3b**, C_3^s of **2a** and C_2^s of **3a** are dominated by two OFs which correspond to the excitation pattern of the α-band in the UV spectra of alternant hydrocarbons [24]. On the other hand C_1^s of **3a** and C_2^s of **3b** are dominated by one OF corresponding to the p-band (HOMO → LUMO) excitation pattern [24]. The approximate validity of the pairing theorem [23] even within the framework of the INDO approach is demonstrated by the almost equal weight of the OFs $\phi_{42} \rightarrow \phi_{44}$ and $\phi_{41} \rightarrow \phi_{43}$ in C_1^s of **1a** and particular of **1b**. The second singlet roots λ_2^s if **1a**/**b** or **1** with π-SCF bond lengths are only slightly higher in energy than λ_1^s. The corresponding eigenfunctions C_2^s describe p-band type OFs similar as C_1^s of **3a** and C_2^s of **3b**.

The two eigenfunctions $C_{1,2}^s$ of **2a** with $n \rightarrow \pi^*$ character consist predominantly of OFs from the non-bonding orbitals n_+ and n_- to virtual π-orbitals, cf. Fig. 3. These n-orbitals are near-degenerate and their energy does not depend significantly on the chosen geometrical model. On the other hand the energy differences between the highest occupied and lowest virtual π-orbitals are much smaller for **2b** than for **2a**. Consequently the change in geometry from **2a** to **2b** reduces the energies of the $\pi \rightarrow \pi^*$ OFs to a larger extent than those of the $n \rightarrow \pi^*$ OFs so that for **2b** the $\pi \rightarrow \pi^*$ OFs can determine C_1^s. All eigenfunctions C_i^s with the lower roots λ_i^s of the singlet instability problem (1) given in Table 1 describe solutions of the charge density wave type since all occurring OFs are symmetry breaking.

Also the lowest roots λ_1^c of the non-real (complex) instability problem for all studied compounds are well above zero and even within the η-criterion the INDO HF wave functions are lower in energy than complex solutions of the HF equations. All associated eigenfunctions C_1^s are dominated by one OF with the $\pi \rightarrow \pi^*$ type $\phi_h \rightarrow \phi_l$ excitation (p-band pattern), only with **2b** it is the $\phi_{h-1} \rightarrow \phi_l$ excitation. Similar to the singlet instability roots the complex root λ_1^c is at least 1.2 eV lower for the aromatic models **Xb** than for the olefinic ones **Xa** and this applies as well to the lowest roots λ_1^t of the non-singlet (triplet) instability problem. The olefinic geometrical models are characterized either by a vanishing triplet root λ_1^t (**1a**), which will become negative if one takes into account all possible OFs, or small positive λ_1^t (**2a**, **3a**) whereas $\lambda_1^t \ll 0$ and $\lambda_2^t < 0$ is obtained for all aromatic models **Xb**. For **1** with the bond lengths taken from the π-SCF calculation only the lowest triplet root λ_1^t is negative. Therefore in all cases exist unrestricted HF solutions with either lower (**1**, **2b**, **3b**) or similar energy (**2a**, **3a**) than the restricted HF energy. The eigenfunctions C_1^t associated with λ_1^t violate the spin and the spatial symmetry. Different to the non-real instability problem C_1^t is now dominated in all compounds by the HOMO → LUMO OF.

Table 1. HOMO-LUMO gaps g and results of the singlet, non-real and non-singlet instability calculations of **1**–**3** according to the INDO method; the instability roots λ_j^a, the OFs, their contributions to the roots, and their type and symmetry, as well as the corresponding diagonal matrix elements $M_{ik,ik}^a$ are also given. All energy values in units of eV

Compound	g	λ_j^s	$\phi_i \rightarrow \phi_k$	(%)	Type	Γ	$M_{ik,ik}^s$	λ_j^c	$\phi_i \rightarrow \phi_k$	(%)	Type	Γ	$M_{ik,ik}^c$	λ_j^t	$\phi_i \rightarrow \phi_k$	(%)	Type	Γ	$M_{ik,ik}^t$
1a	6.91	3.09	42→44	(49.1)	$\pi\pi^*$	B_{1g}	3.97	2.50	42→43	(84.3)	$\pi\pi^*$	B_{3u}	2.92	0.00	42→43	(61.4)	$\pi\pi^*$	B_{3u}	1.75
			41→43	(35.5)			4.15							1.04	41→43	(34.3)	$\pi\pi^*$	B_{1g}	3.38
		3.21	42→43	(68.3)	$\pi\pi^*$	B_{3u}	4.10								42→44	(33.7)			3.37
1b	4.63	1.54	42→44	(46.9)	$\pi\pi^*$	B_{1g}	2.39	1.24	42→43	(94.0)	$\pi\pi^*$	B_{3u}	1.38	−2.07	42→43	(76.8)	$\pi\pi^*$	B_{3u}	−0.93
			41→43	(43.6)			2.44							−0.43	41→43	(41.5)	$\pi\pi^*$	B_{1g}	1.54
		1.75	42→43	(55.3)	$\pi\pi^*$	B_{3u}	3.70								42→44	(39.2)			1.63
			41→44	(28.4)			4.48							0.08	42→45	(45.2)	$\pi\pi^*$	A_g	1.92
															40→43	(34.2)			2.18
1[a]	5.94	2.48	42→44	(49.1)	$\pi\pi^*$	B_{1g}	3.29	1.89	42→43	(89.1)	$\pi\pi^*$	B_{3u}	2.18	−0.86	42→43	(62.7)	$\pi\pi^*$	B_{3u}	0.66
			41→43	(38.3)			3.42							0.49	41→43	(37.4)	$\pi\pi^*$	B_{1g}	2.61
		2.55	42→43	(67.0)	$\pi\pi^*$	B_{3u}	3.70								42→44	(36.5)			2.64
2a	7.46	2.98	40→43	(60.9)	$n_-\pi^*$	B_{3g}	4.20	2.80	42→43	(81.1)	$\pi\pi^*$	B_{3u}	3.25	0.37	42→43	(62.1)	$\pi\pi^*$	B_{3u}	1.91
			39→46	(29.4)	$n_+\pi^*$		5.81												
		3.01	39→43	(57.6)	$n_+\pi^*$	A_u	4.30												
			40→46	(31.8)	$n_-\pi^*$		5.73												
		3.13	41→43	(61.1)	$\pi\pi^*$	B_{1g}	3.88												
			42→44	(19.7)			4.63												

2b	5.61	1.68	41→43	(79.9)	$\pi\pi^*$	B_{1g}	2.19	1.48	41→43	(94.0)	$\pi\pi^*$	B_{1g}	1.69	−1.45	42→43	(64.3)	$\pi\pi^*$	B_{3u}	−0.18
			42→44	(10.8)				1.69	42→43	(86.5)	$\pi\pi^*$	B_{3u}	1.96		41→44	(18.9)			2.04
														−0.78	41→43	(46.6)	$\pi\pi^*$	B_{1g}	1.19
															42→44	(24.8)			2.30
														0.17	41→44	(24.0)	$\pi\pi^*$	B_{3u}	2.04
															38→43	(21.2)			2.77
3a	6.73	3.11	58→59	(74.8)	$\pi\pi^*$	B_{3u}	3.90	2.46	58→59	(85.5)	$\pi\pi^*$	B_{3u}	2.86	0.20	58→59	(61.9)	$\pi\pi^*$	B_{3u}	1.82
		3.22	57→59	(53.1)	$\pi\pi^*$	B_{1g}	3.95							1.39	58→61	(45.9)	$\pi\pi^*$	A_g	3.33
			58→60	(35.5)			4.11								56→59	(30.6)			3.84
3b	4.26	1.51	57→59	(66.4)	$\pi\pi^*$	B_{1g}	2.07	1.11	58→59	(95.7)	$\pi\pi^*$	B_{3u}	1.22	−1.91	58→59	(79.2)	$\pi\pi^*$	B_{3u}	−0.98
			58→60	(26.5)			2.53							−0.21	57→59	(50.6)	$\pi\pi^*$	B_{1g}	1.34
		1.65	58→59	(59.1)	$\pi\pi^*$	B_{3u}	3.41								58→60	(34.5)			1.85
			57→60	(25.9)			4.45							0.48	58→61	(44.4)	$\pi\pi^*$	A_g	1.90
															56→59	(42.3)			1.88

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[a] With bond lengths obtained by the π-SCF procedure

In the case of the aromatic models **Xb** we can easily demonstrate why a triplet state with violations of the spatial orbitals will be more stable than the HF wave function. Here already the dominant OF $\phi_h \rightarrow \phi_l$ alone leads to a negative λ_1^t since the diagonal matrix element (Eq. (2)) $M^t_{hl,hl} < 0$. Consequently the Fermi gap is limited from above $g < J_{hl} + K_{hl}$. Furthermore we can write $(M^c_{hl,hl} + M^t_{hl,hl})/2 = g - J_{hl} = T_{hl}$ where T_{hl} stands for the triplet transition energy with respect to the HF energy of a triplet configuration characterized by the one-electron excitation $\phi_h \rightarrow \phi_l$. From Table 1 we obtain $T_{hl} = 0.23$, 0.89 and 0.12 eV for **1b**, **2b** and **3b**. Clearly this triplet configuration $\phi_h \rightarrow \phi_l$ will mix with others $\phi_i \rightarrow \phi_k$ and then the off-diagonal coupling is given by the mean of $M^t_{hl,ik}$ and $M^c_{hl,ik}$ (Eq. (3)) [24]. Thus the magnitude of the reduction of the energy of the triplet state with the dominant $\phi_h \rightarrow \phi_l$ excitation will be approximately the mean of $(M^c_{hl,hl} - \lambda_1^c)$ (respectively $(M^c_{hl,hl} - \lambda_2^c)$ in the case of **2b**) and $(M^t_{hl,hl} - \lambda_1^t)$. Taking the corresponding values given in Table 1 we can estimate that these reductions will exceed the T_{hl} values. Thus this triplet state will be more stable than the HF wave function. It should be stressed that this is not tantamount to a triplet ground state of such a system since electron correlation stabilizes the HF wave function more than the triplet state. A corresponding analysis for the olefinic models **Xa** reveals markedly larger T_{hl} values in the range 2.3–2.5 eV and hence λ_1^t roots are larger as well compared with those of the aromatic models **Xb**.

The lowest roots λ_1^a of all three instability problems (1) turned out to be significantly smaller in the aromatic structures **Xb** than in the corresponding olefinic ones **Xa**. The same applies to the differences $\lambda_1^s - \lambda_1^t$ which signifies the greater importance of ferromagnetic spin-correlation in the aromatic geometries. This finding is plausible since **Xb** represents a highly delocalized π-system whereas alternating formal single and double bonds in **Xa** induce the formation of weakly interacting electron pairs to a certain extent. The difference between λ_1^a(**Xa**) and λ_1^a(**Xb**) stems mainly from the different HOMO-LUMO gaps. In the aromatic models **Xb** the HOMO-LUMO gaps g are of similar magnitude as the Coulomb integrals J_{hl} so that in connection with large exchange integrals K_{hl} according to Eq. (2) negative $M^t_{hl,hl}$ and λ_1^t values are obtained. The reason for the large Coulomb and exchange integrals with respect to HOMO and LUMO is the approximate validity of the pairing theorem in these compounds.

5. HF instabilities of the π-SCF wave functions

The π-SCF HOMO-LUMO gaps g are considerably smaller than the INDO gaps and decrease similarly according to $\mathbf{2} > \mathbf{1} > \mathbf{3}$, cf. Table 2. Due to these extreme low g values we have to expect HF instabilities. Indeed we find triplet instabilities for **1–3** since $\lambda_1^t < 0$. The lowest roots λ_1^s and λ_1^c of the singlet and non-real (complex) instability problem are well above zero for all studied compounds similar as within the INDO approach. Consequently there exist neither other wave functions with closed shell character nor complex solutions of the HF equations which are lower in energy than the restricted HF solution. The comparison of Table 1 and 2 reveals that the eigenfunctions C_1^c and C_1^t obtained

Table 2. HOMO-LUMO gaps g and results of the singlet, non-real and non-singlet instability calculations of **1**–**3** according to the π-SCF method. Legend see Table 1

Compound	g	λ_j^s	$\phi_i \rightarrow \phi_k$	(%)	Γ	$M^s_{ik,ik}$	λ_j^c	$\phi_i \rightarrow \phi_k$	(%)	Γ	$M^c_{ik,ik}$	λ_j^t	$\phi_i \rightarrow \phi_k$	(%)	Γ	$M^t_{ik,ik}$
1	3.42	2.27	9 → 10	(60.4)	B_{3u}	4.01	1.10	9 → 10	(98.8)	B_{3u}	1.13	−3.26	9 → 10	(71.3)	B_{3u}	−1.74
			8 → 11	(32.8)		4.94										
		2.34	9 → 11	(47.6)	B_{1g}	2.60										
			8 → 10	(47.6)		2.60										
2	3.98	1.74	8 → 10	(97.2)	B_{1g}	1.91	1.22	8 → 10	(97.5)	B_{1g}	1.31	−2.83	9 → 10	(65.7)	B_{3u}	−1.15
3	2.47	0.98	12 → 14	(98.0)	B_{1g}	1.07	0.64	13 → 14	(99.6)	B_{1g}	0.65	−2.35	13 → 14	(81.9)	B_{3u}	−1.74
		1.69	13 → 14	(71.4)	B_{3u}	3.04										

with the INDO and the π-SCF Hamiltonian are dominated by the same type of OFs. The same is true for the eigenfunctions C_i^s of the singlet instability problem with $\pi \rightarrow \pi^*$ nature which are related to the lowest λ_i^s given in Table 1 and 2 if we disregard their order in the case of the nearly degenerate first two eigenfunctions of **1** and **3a**.

The preselection of configurations has proved indispensable with the studied compounds in order to obtain the true HF wave function. Otherwise the INDO procedure diverges for **2b** and the π-SCF procedure yields a wave function for **3** which is singlet unstable due to a negative λ_1^s caused by a negative $M^s_{hl,hl}$ diagonal matrix element for the HOMO→LUMO ($\phi_h \rightarrow \phi_l$) OF. According to Ref. [25] convergence difficulties in the classical SCF-algorithmus are to be expected if the following conditions are fulfilled: (i) singlet instability is present, (ii) the matrix $D^{1/2}SD^{1/2}$ has only eigenvalues $\delta < 1$. The matrix elements of D and S are given as $D_{ik,jl} = \delta_{ik}\delta_{jl}(\varepsilon_k - \varepsilon_i)^{-1}$ and $S_{ik,jl} = -M^s_{ik,jl} - D^{-1}_{ik,jl}$. Although we do not use extrapolation or dumping procedures in our π-SCF method no convergence problems were encountered. This can be rationalized if we define $M = M^s_{hl,hl}$ and equate $M = D^{-1} - S$ where D and S are now 1×1 matrices since we consider only the $\phi_h \rightarrow \phi_l$ OF. We obtain $(M + S)D = 1$ and hence $\delta = D^{1/2}SD^{1/2} = SD$. Since $M < 0$ it is $SD > 1$ and consequently $\delta > 1$. Thus condition (ii) is not fulfilled in contrast to most other molecules [25] and SCF convergence becomes possible although the wave function is singlet unstable.

6. Conclusions

The electronic structures and the Thouless instabilities of the extended conjugated π-electron acceptors **1–3** have been investigated by means of semiempirical INDO and π-SCF Hamiltonians. For the TCNQ analogue TCNP **3** one expects [2] an EA superior to that of TCNQ. The EA of a molecule with N electrons is a property of the corresponding $(N+1)$ electron system whereas the IP is determined by the $(N-1)$ electron system. Correlations between the N electron HF wave function and EA or IP are obtained only via Koopmans' theorem. However, there is some evidence [14, 26] that in the case of planar conjugated compounds such simple correlations are satisfactory. Therefore we can assume that our calculated electronic structures of the HF ground states of **1–3** and the derived IPs and EAs are reliable as long as the investigation of the Thouless stability conditions proved the independent particle model to be a sufficient approximation.

The INDO and π-SCF HF wave functions for **1–3** exhibit lowest roots of the singlet instability problem well above zero. Therefore the mean-field approach of the HF procedure is a sufficient approximation to the ground state which is not governed by correlation effects. The additional non-real stability means that we can consider our real HF wave functions as adequate representations of the ground states of **1–3**, but the occurrence of (near) non-singlet instabilities underlines the importance of spin correlation in these systems and demonstrates that a treatment of excited states and their energies with respect to the ground state is possible only by inclusion of additional configuration interaction for ground and excited states.

The INDO calculations showed that IPs and EAs of **1**–**3** depend considerably on the chosen geometrical model, the differences between olefinic and aromatic structures **Xa** and **Xb** amount to 1.0–1.5 eV. The π-SCF results for **1**–**3** correspond to a geometry intermediate of the olefinic and aromatic model. According to our results the replacement of $X = CH_2$ (**1**) by the better acceptor function $X = O$ (**2**) and $X = C(CN)_2$ (**3**) leads to the expected increase of EA and hence to a better acceptor capability. We predict $EA \cong 2.5$, 3.4 and 3.6 eV for **1**, **2** and **3** from our INDO calculations if we assume that the mean value of the EAs for the olefinic and aromatic structure corresponds to that obtained for the optimum geometry. Taking the π-SCF bond lengths for **1** we calculate $EA \cong 2.4$ eV in almost agreement with the mean value of **1a** and **1b**. It is interesting to note that simple Hückel-type calculations predict a similar $EA \cong 3.4$ eV for **3** [27]. The π-SCF method together with Eq. (12) of Ref. [14] gives a somewhat smaller $EA = 1.8$ and 2.7 eV for **1** and **2** but a slightly larger $EA = 4.1$ eV for **3**. Both theoretical approaches predict a better acceptor capability for **3** with respect to that of TCNQ [22]. In contrast to the π-SCF results the difference in EA of **2** and **3** as obtained with the INDO Hamiltonian turns out significantly smaller than one would expect based on the comparison with the related acceptors *p*-benzoquinone and TCNQ [22]. There is an increase from **1** and **2** of EA and IP but the further increase of EA from **2** to **3** is accompanied by a decrease (INDO) or near-constancy (π-SCF) of IP. Therefore the HOMO-LUMO gap of **3** is considerably smaller than that of **2** which indicates higher reactivity of **3** with respect to **2**.

Finally we want to stress the importance of checking the reliability of quantum chemical calculations on compounds which are expected to exhibit extreme molecular properties, e.g. small HOMO-LUMO gaps or extreme large EAs or small IPs. The investigation of the stability of the HF wave function by means of the Thouless stability conditions constitutes a bridge between the independent particle model and approaches beyond the mean-field approximation which are very often not feasible with larger systems.

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