

Synthesis and Characterization of 11,11,12,12-Tetracyano-1,4-anthraquinodimethanes (1,4-TCAQs): Novel Electron Acceptors with Photoinduced Charge-Transfer Properties

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The synthesis of novel substituted 11,11,12,12-tetracyano-1,4-anthraquinodimethanes (1,4-TCAQs) **3** from the corresponding 1,4-anthraquinones **2** by reaction with the Lehnert's reagent is described, thus confirming the validity of this procedure to obtain different substitution patterns on the benzene fused quinone ring. UV-vis spectra of the novel compounds show the presence of an intramolecular charge-transfer band in the blue part of the visible region. Depending upon the substitution pattern, the cyclic voltammetry (CV) measurements on 1,4-TCAQs reveal one reduction wave involving two electrons to the dianion or two one-electron reduction waves to the corresponding radical-anion and dianion. Acceptor properties similar to those of TCNQ are expected for **3** when the TCNQ moiety is substituted with chlorine atoms. The molecular and electronic structures of compounds **2** and **3** are investigated using the semiempirical PM3 method and the nonempirical VEH approach, respectively. PM3 calculations predict that 1,4-TCAQs are nonplanar and adopt a butterfly-type structure where the planarity of the lateral naphthalene unit is preserved. VEH calculations show that the naphthalene moiety behaves as an electron donor since the HOMO → LUMO transition corresponds to an electronic charge transfer from this moiety to the acceptor TCNQ ring, thus supporting the experimental UV-vis results. The evolution of the geometric structure of compounds **3** upon reduction evidences a gain of aromaticity of the TCNQ ring, even if the anions are predicted to remain nonplanar. This absence of planarity justifies the low stability found experimentally for the anions and explains the observation of only one reduction wave involving two-electrons for the most hindered derivatives.

Introduction

Tetracyano-*p*-quinodimethane (TCNQ) (**1**) is a very well-known molecule because it reacts with the strong electron donor molecule tetrathiafulvalene (TTF) to form a π -molecular charge-transfer complex (TTF-TCNQ) exhibiting high electrical conductivity.¹ Recently, TCNQ has also been proposed as a potential system for molecular electronic devices,² organic ferromagnets,³ and nonlinear optical compounds.⁴

The difficulties in obtaining novel TCNQ derivatives arise from the fact that their earlier syntheses usually

involved multistep highly toxic processes.⁵ A decade ago, the use of the Lehnert's⁶ reagent allowed the direct preparation of novel substituted TCNQs from quinones.⁷ However, the reaction fails with some quinones⁸ and seems to be only applicable to tetrasubstituted derivatives.⁹ Consequently, some recently described TCNQ derivatives were prepared from non-quinone starting materials in several synthetic steps.^{10,11}

In previous papers,^{12,13} we have described the synthesis of π -extended TCNQ derivatives from the corresponding

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(1) Ferraris, J.; Cowan, D. O.; Walatka, V. V.; Perlstein, J. H. *J. Am. Chem. Soc.* **1973**, *95*, 948. Coleman, L. B.; Cohen, M. J.; Sandman, D. J.; Yamagishi, F. G.; Garito, A. F.; Heeger, A. J. *Solid State Commun.* **1973**, *12*, 1125.

(2) Metzger, R. M.; Schumaker, R. R.; Cava, M. P.; Laidlaw, R. K.; Panetta, C. A.; Torres, E. *Langmuir* **1988**, *4*, 298. Metzger, R. M.; Panetta, C. A. *New J. Chem.* **1991**, *15*, 209. Panetta, C. A.; Heimer, N. E.; Hussey, C. L.; Metzger, R. M. *Synlett* **1991**, 301.

(3) Miller, J. S.; Epstein, A. J.; Rieff, W. M. *Chem. Rev.* **1988**, *88*, 201. Miller, J. S.; Calabrese, J. C.; Harlow, R. L.; Dixon, D. A.; Zhang, J. H.; Rieff, W. M.; Chittipeddi, S.; Selover, M. A.; Epstein, A. J. *J. Am. Chem. Soc.* **1990**, *112*, 5496.

(4) Ashwell, G. J.; Dawney, E. J. C.; Kuczynski, A. P.; Szablewski, M.; Sandy, I. M.; Bryce, M. R.; Grainger, A. M.; Hasan, M. *J. Chem. Soc. Faraday Trans.* **1990**, *86*, 1117.

(5) Sandman, D. J.; Garito, A. F. *J. Org. Chem.* **1974**, *39*, 1165. Wheland, R. C.; Martin, E. L. *J. Org. Chem.* **1975**, *40*, 3101. Addison, A. W.; Dalal, N. S.; Hoyano, Y.; Huizinga, S.; Weiler, L. *Can. J. Chem.* **1977**, *55*, 4191. Maxfield, R.; Cowan, D. O.; Bloch, A. N.; Poehler, T. O. *Nouv. J. Chim.* **1979**, *3*, 647. Acton, N.; Hou, D.; Schwarz, J.; Katz, T. J. *J. Org. Chem.* **1982**, *47*, 1011.

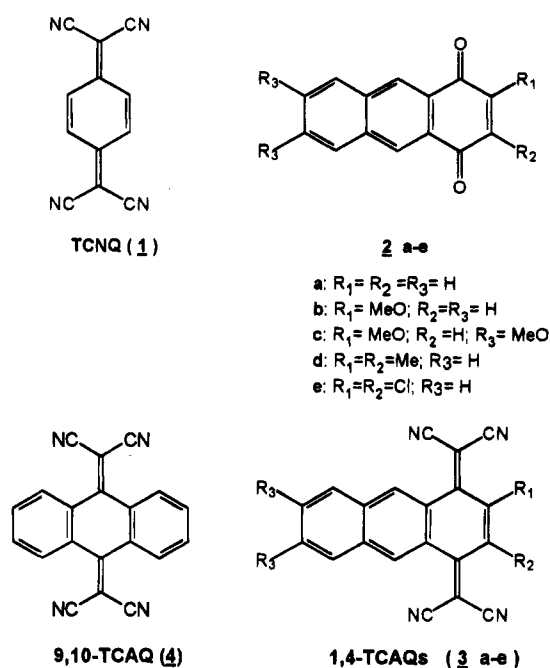
(6) Lehnert, W. *Tetrahedron Lett.* **1970**, 4723. Lehnert, W. *Synthesis* **1974**, 667.

(7) Ong, B. S.; Keoshkerian, B. *J. Org. Chem.* **1984**, *49*, 5002. Aumuller, A.; Hünig, S. *Liebigs Ann. Chem.* **1984**, 618. Torres, E.; Panetta, C. A.; Metzger, R. M. *J. Org. Chem.* **1987**, *52*, 2944.

(8) Bryce, M. R.; Davies, S. R.; Grainger, A. M.; Hellberg, J.; Hursthouse, M. B.; Mazid, M.; Bachmann, R.; Gerson, F. *J. Org. Chem.* **1992**, *57*, 1690. Becker, J. Y.; Bernstein, J.; Bittner, S.; Harlev, E.; Sharma, J. A. R. P. *J. Chem. Soc. Perkin Trans. 2* **1989**, 1157. Czekanski, T.; Hanack, M.; Becker, J. Y.; Bernstein, J.; Bittner, S.; Kaufman-Orenstein, L.; Peleg, D. *J. Org. Chem.* **1991**, *56*, 1569.

(9) Martín, N.; Hanack, M. *J. Chem. Soc. Chem. Commun.* **1988**, 1522. Kini, A.; Mays, M.; Cowan, D. O. *J. Chem. Soc. Chem. Commun.* **1985**, 286. See also references 7 and 12.

Scheme 1



quinones and discussed their acceptor ability in terms of steric and electronic effects. To the best of our knowledge, only the parent nonsubstituted 11,11,12,12-tetracyano-1,4-anthraquinodimethane (1,4-TCAQ) has previously been reported. It was obtained in a very poor total yield (5.4%) from 1,4-bis(bromomethyl)anthracene using a multistep procedure.¹⁴

In this paper we report the synthesis of TCNQ derivatives from substituted 1,4-anthracenediones **2** by using the Lehnert's reagent (malononitrile, TiCl₄, pyridine).¹⁵ The novel 11,11,12,12-tetracyano-1,4-anthraquinodimethanes (1,4-TCAQs) **3** prepared by this procedure prove the validity of the Lehnert's conditions to prepare tetra- or trisubstituted TCNQ derivatives.

Theoretical studies suggested that the extension of the π -system of the TCNQ ring would result in a lowering of the intramolecular Coulomb repulsion leading to highly conducting CT complexes.¹⁶ However, when the π -system is extended laterally, the steric hindrance of the aromatic *peri* hydrogens with the dicyanomethylene groups of the TCNQ moiety results in highly distorted molecules exhibiting poor acceptor abilities.^{7,12,13} We have undertaken the synthesis of different derivatives of the π -extended molecule 1,4-TCAQ bearing in mind that the geometry of these acceptors is less hindered than for the

2,3-5,6 benzene-fused TCNQ derivatives previously described.^{7,12,13} They should therefore present a better planarity similar to that observed for the less extended 9,9,10,10-tetracyano-1,4-naphthoquinodimethane (benzo-TCNQ).¹⁷ The presence of different substituents in 2,3-positions on the TCNQ moiety allows to tune the acceptor capacity of these molecules. Molecular orbital calculations have been performed in order to gain information about the planarity of these compounds and to rationalize their electrochemical behavior.

Results and Discussion

Synthesis. The novel acceptors (1,4-TCAQs, **3a-e**) were prepared from the corresponding substituted 1,4-anthracenediones **2**¹⁸ by reaction with malononitrile in the presence of titanium tetrachloride (Lehnert's reagent). Compounds **3** were thus obtained as stable microcrystalline red solids in moderate to good yields. They were purified by fractional crystallization or by flash chromatography using florisil as the adsorbent (see Experimental Section). It is worth mentioning that the unsubstituted 1,4-TCAQ (**3a**: R₁ = R₂ = R₃ = H) could also be prepared by following this procedure from the corresponding 1,4-anthracenedione (**2a**: R₁ = R₂ = R₃ = H) as a red solid in 58% crude yield (IR: $\nu_{\text{CN}} = 2220 \text{ cm}^{-1}$; no C=O band). However, all attempts to purify this solid (flash chromatography using silica-gel or florisil, preparative TLC, sublimation, or fractional recrystallization) led to extensive hydrolysis of the exocyclic double bond, yielding the starting yellow quinone (TLC). Even in this case, in which the 2,3-benzene fused TCNQ ring resulted to be highly reactive toward hydrolysis, the Lehnert's reagent proved to be useful to form the TCNQ derivative.

The UV-vis spectra of 1,4-TCAQs (**3**) show the presence of a low-energy absorption band in the visible region (λ_{max} ca. 440–500 nm) in addition to the expected bands in the UV region. The band in the visible is bathochromically shifted when the naphthalene moiety bears electron-releasing methoxy substituents (Figure 1). This finding suggests an intramolecular charge transfer from the donor naphthalene moiety to the acceptor TCNQ ring of the molecule.

Electrochemistry. The electrochemical properties of compounds **2** and **3** were studied by cyclic voltammetry (CV) at room temperature. The half-wave redox potentials are summarized in Table 1. The CV reduction potentials measured in the same experimental conditions for the parent TCNQ and those previously reported for benzo-TCNQ¹⁹ are included for comparison purposes.

The 1,4-TCAQs derivatives show a different electrochemical behavior depending upon the substitution degree. Thus, compounds **3b** and **3c** bearing three substituents on the TCNQ ring exhibit two one-electron reversible reduction waves to the corresponding anion-radicals and dianions. The difference between the first and second reduction potentials (ΔE) has a small value compared with that found for the parent TCNQ molecule. This is due to the more negative first reduction potentials measured for **3b** and **3c**. Furthermore, the low values

(10) Bryce, M. R.; Grainger, A. M.; Hassan, M.; Ashwell, G. J.; Bates, P. A.; Hursthouse, M. B. *J. Chem. Soc., Perkin Trans 1* **1992**, 611. Bryce, M. R.; Hassan, M.; Ashwell, G. J. *J. Chem. Soc., Chem. Commun.* **1989**, 529.

(11) Martín, N.; Segura, J. L.; Seoane, C.; Albert, A.; Cano, F. H. *J. Chem. Soc., Perkin Trans 1* **1993**, 2363.

(12) Martín, N.; Behnisch, R.; Hanack, M. *J. Org. Chem.* **1989**, *54*, 2563. Martín, N.; Seoane, C.; Segura, J. L.; Marco, J. L.; Hanack, M. *Synth. Met.* **1991**, *42*, 1873. Cruz, P.; Martín, N.; Miguel, F.; Seoane, C.; Albert, A.; Cano, F. H.; Leverenz, A.; Hanack, M. *Synth. Met.* **1992**, *48*, 59. Cruz, P.; Martín, N.; Miguel, F.; Seoane, C.; Albert, A.; Cano, F. H.; González, A.; Pingarrón, J. M. *J. Org. Chem.* **1992**, *57*, 6192.

(13) Bando, P.; Martín, N.; Segura, J. L.; Seoane, C.; Albert, A.; Cano, F. H.; Ortí, E.; Viruela, P.; Viruela, R. *J. Org. Chem.* **1994**, *59*, 4618.

(14) Yamaguchi, S.; Tatemitsu, H.; Sakata, Y.; Misumi, S. *Chem. Lett.* **1983**, 1229.

(15) A part of this paper was presented as a communication in the International Conference on Science and Technology on Synthetic Metals, ICMS92, August, 1992, Göteborg, Sweden.

(16) Garito, A. F.; Heeger, A. J. *Acc. Chem. Res.* **1974**, *7*, 232.

(17) Iwasaki, F. *Acta Crystallogr. B* **1971**, *27*, 1360.

(18) Barranco, E.; Martín, N.; Segura, J. L.; Seoane, C.; Cruz, P.; Langa, F.; González, A.; Pingarrón, J. M. *Tetrahedron* **1993**, *49*, 4881 and references cited therein.

(19) Kini, A. M.; Cowan, D. O.; Gerson, F.; Möckel, R. *J. Am. Chem. Soc.* **1985**, *107*, 556.

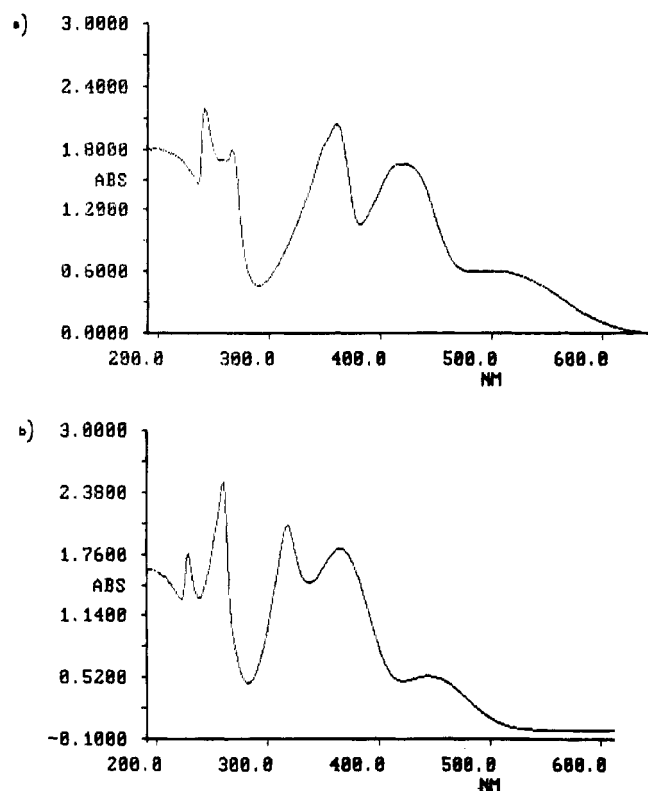


Figure 1. UV-vis spectra of compounds **3c** (a) and **3d** (b) in CHCl_3 .

Table 1. Cyclic Voltammetry Data of Novel Acceptors (V vs SCE)^a

compound	$E^{1/2}$	$E^{2/2}$	ΔE	$\log K^b$
2a	-0.57	-1.13	0.56	9.49
2b	-0.73	-1.23	0.50	8.47
2c	-0.74	-1.24	0.50	8.47
2d	-0.64	-1.16	0.52	8.81
2e	-0.42	-0.90	0.48	8.13
3a^c	-0.18	-0.48	0.30	5.17
3b	-0.12	-0.31	0.19	3.27
3c	-0.11	-0.29	0.18	3.10
3d	-0.17 (2e)			
	-0.22 (2e) ^d			
3e	0.16 (2e)			
	0.02 (2e) ^d			
TCNQ ^e	0.19	-0.36	0.55	9.65
benzo-TCNQ ^f	-0.26	-0.74	0.48	8.27

^a Versus Ag wire as Ag/Ag^+ quasireference electrode; electrolyte $\text{Bu}_4\text{N}^+\text{ClO}_4^-$; solvent MeCN; scan rate 20 mV s^{-1} . ^b $\log K = \Delta E / 0.058$. ^c Data from reference 14; solvent MeCN. ^d Solvent CH_2Cl_2 . ^e Measured in the same experimental conditions. ^f Data from reference 19; solvent MeCN.

obtained for $\log K$ (see Table 1)²⁰ reveal that the anion-radicals of **3b** and **3c** have a very poor thermodynamic stability compared with the anion-radical of TCNQ. The low stability is probably due to the lack of planarity of the anion-radicals and will be discussed below. These trends are confirmed for the tetrasubstituted TCNQ derivatives **3d** and **3e** which show only one reversible reduction wave to the dianion. The separation between the anodic and cathodic peaks, less than 60 mV, suggests a two-electron transfer. The lower stability of the anion-radicals for the tetrasubstituted TCNQ ring of compounds

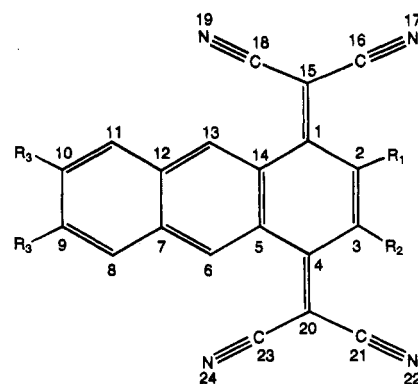


Figure 2. Atom numbering used for 1,4-TCAQs.

3d and **3e** is responsible of the coalescence of the first and second reduction waves into a single one.

The CV data for the starting quinones are also presented in Table 1. All the quinones **2a–e** show two one-electron reversible reduction waves shifted, as expected, toward more negative values with regard to the respective 1,4-TCAQs.

Substitution on the TCNQ ring in compounds **3** allows tuning of the acceptor ability depending upon the electronic behavior of the substituents. Thus, compound **3e** bearing two chlorine atoms shows the best acceptor properties, exhibiting a two-electron reduction potential close to that of the parent TCNQ molecule (see Table 1). This result suggests that compound **3e** could be a good candidate to form charge-transfer complexes with electron donors where the acceptor molecules accept more than one electron. On the other hand, substitution on the hydrocarbon framework does not alter significantly the reduction potentials. This fact is in agreement with the location of the negative charges in the anion-radical and dianion mainly on the two dicyanomethylene groups.²¹ It should be finally mentioned that the coalescence of the two first reduction waves has been already observed for the closely related 11,11,12,12-tetracyano-9,10-anthraquinodimethane (9,10-TCAQ, **4**)²¹ and 15,15,16,16-tetracyano-6,13-pentacenequinodimethane (TCPQ)¹² molecules, for tetramethyltetracyano-*p*-quinodimethane (TMTCNQ)²² which is also nonplanar,²³ and for other similar systems including heteroatoms.¹³ The main difference with the TCNQ derivatives presented in this work is that 1,4-TCAQs have more positive reduction potentials (9,10-TCAQ has a reduction potential of -0.46 V^{21} and TCPQ of -0.57 V^{12}) and equals the acceptor properties of TCNQ in the case of **3e**.

Theoretical Calculations. The geometric and electronic structures of quinones **2** and 1,4-TCAQ derivatives **3** were investigated by performing molecular-orbital calculations. In the following discussion we mainly focus on the results obtained for 1,4-TCAQs, the properties calculated for quinones **2** being invoked only for the sake of comparison. The atomic numbering used in this section corresponds to that depicted in Figure 2.

Neutral Compounds: Geometric Structure. The molecular geometries of compounds **2** and **3** were fully optimized using the PM3 semiempirical method. This

(20) K is the coproportionation constant for the equilibrium $\text{A} + \text{A}^{2-} \rightleftharpoons 2\text{A}^-$, and the value of $\log K$ is calculated from the difference between the two first reduction potentials ($\Delta E = E^{1,\text{red}}_{1/2} - E^{2,\text{red}}_{1/2}$). Jensen, B. S.; Parker, U. D. *J. Am. Chem. Soc.* **1975**, *97*, 5211.

(21) Gerson, F.; Heckendorn, R.; Cowan, D. O.; Kini, A. M.; Maxfield, M. J. *Am. Chem. Soc.* **1983**, *105*, 7017. See also ref 12.

(22) Kini, A.; Mays, M.; Cowan, D. O. *J. Chem. Soc., Chem. Commun.* **1985**, 286.

(23) Rosenau, B.; Krieger, C.; Staab, H. A. *Tetrahedron Lett.* **1985**, *26*, 2081.

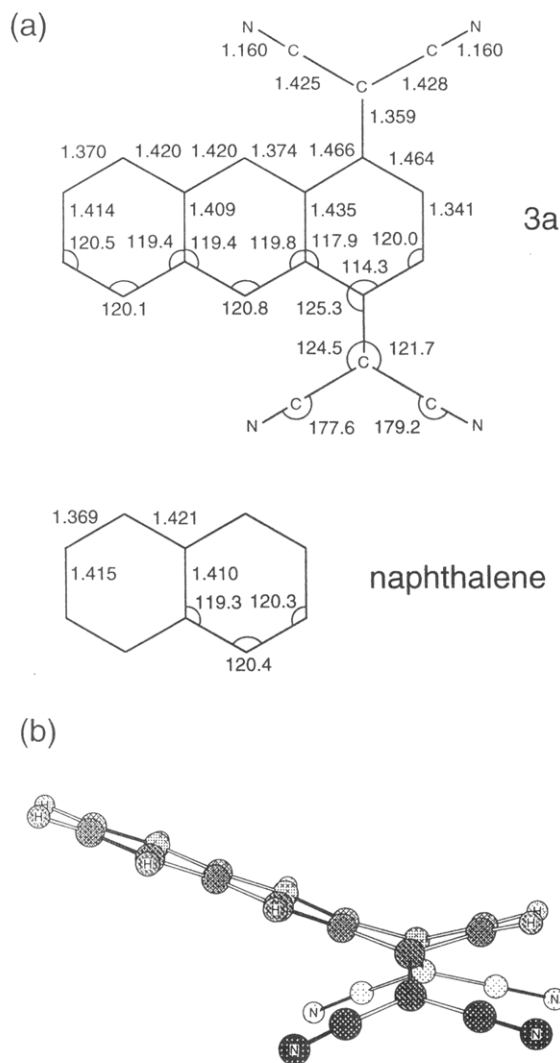


Figure 3. (a) Most significant PM3-optimized bond lengths (Å) and bond angles (deg) calculated for 1,4-TCAQ (**3a**) and naphthalene. (b) Lateral view showing the minimum energy nonplanar conformation adopted by **3a**.

method has been previously applied to the study of π -extended TCNQ derivatives for which it has been shown to provide molecular geometries in very good agreement with crystallographic X-ray data.¹³ The plane bisecting perpendicularly the C2–C3 and C9–C10 bonds was assumed to be a symmetry plane (C_s symmetry) during the optimization process except for compounds **2b,c** and **3b,c** for which no symmetry restriction was imposed. Figure 3 displays the PM3 equilibrium structure calculated for nonsubstituted 1,4-TCAQ (**3a**). The PM3 geometry optimized for the naphthalene molecule (D_{2h} symmetry) is included in Figure 3 for comparison.

Three main results are inferred from Figure 3: (i) The bond lengths and bond angles calculated for the lateral naphthalene unit of 1,4-TCAQ are identical to those obtained for the naphthalene molecule. This result indicates that the structural identity (geometry and aromaticity) of naphthalene is preserved in 1,4-TCAQ. The consequence of this result on the electronic properties is discussed below. (ii) The TCNQ ring retains its quinoid character showing an important bond length alternation. The lengths computed for bonds C2–C3 (1.341 Å), C2–C1 (1.464 Å), and C1–C15 (1.359 Å) are very similar to those calculated for the parent TCNQ molecule using the same methodology (1.345, 1.456, and 1.362 Å, respectively). (iii)

Table 2. PM3-Optimized Angles (in degrees) Defining the Molecular Distortion from Planarity of 1,4-TCAQ Derivatives (**3**) and of Their Respective Anions.^a The Values Obtained for 9,10-TCAQ (**4**) are Included for Comparison

compound	α	γ
3a	147.3	28.1
3b ^b	143.0	34.8(28.8)
3d	137.1	37.7
3e	141.9	32.9
4	138.3	36.4
3a ⁻	162.0	15.0
3b ⁻	157.3	20.1(17.6)
3d ⁻	147.5	27.3
3e ⁻	153.9	21.7
4 ⁻	145.9	29.2

^a Angle α is calculated as the average of the dihedral angles C2–C1–C4–C5 and C3–C4–C1–C14. Angle γ is averaged over the C15–C2–C14–C5 and C15–C14–C2–C3 dihedral angles. See Figure 2 for atom numbering. ^b Two different values are obtained for γ in asymmetrically substituted **3b** and **3c**. That within parentheses corresponds to the less hindered C(CN)₂ group. The angles calculated for **3c** are identical to those obtained for **3b** and are not included.

1,4-TCAQ is predicted to show a butterfly-type structure similar to that found from experimental X-ray data²⁴ and PM3 calculations¹³ for its structural isomer 9,10-TCAQ. The distortion from planarity is due to the steric interaction between the cyano groups and the CH units in adjacent *peri* positions. To avoid these interactions, the TCNQ ring and the dicyanomethylene units are folded in opposite directions and a boat conformation is therefore obtained for the TCNQ ring. It is to be noted that these distortions do not affect the planarity of the naphthalene unit. All these trends stand for the whole set of 1,4-TCAQ derivatives (**3a–e**) studied in this work.

The introduction of substituents in **3a** induces very small changes in bond lengths and bond angles and mainly affects the degree of distortion from planarity of the molecule. Table 2 lists the theoretical values calculated for the angles describing the molecular distortions from planarity. α Corresponds to the angle formed by the “wings of the butterfly”, i.e. to the dihedral angle C2–C1–C4–C5. γ Defines the angle of tilting of the dicyanomethylene units with respect to the C2–C3–C5–C14 plane. For unsubstituted 1,4-TCAQ (**3a**), α and γ are found to have values of 147.3° and 28.1°, respectively. These values are respectively larger and smaller than those calculated for 9,10-TCAQ ($\alpha = 138.3^\circ$, $\gamma = 36.4^\circ$), indicating that 1,4-TCAQ is significantly less folded than 9,10-TCAQ. The larger folding of the latter is determined by the existence on both sides of the TCNQ ring of nonbonding steric interactions between cyano groups and CH units in *peri* positions (see Scheme 1). These interactions are only present on one side of the TCNQ ring for 1,4-TCAQ. As discussed below, the degree of folding, i.e., the relative importance of the nonbonding interactions, plays a crucial role in determining the different electrochemical behavior shown by 1,4- and 9,10-TCAQ.

When theoretically calculated molecular structures are compared with those obtained from X-ray solid-state data it should be borne in mind that theoretical calculations are performed on isolated systems without taking into account the forces involved in the crystal. In this way, the theoretical values calculated for angles α (147.3°) and γ (28.1°) of **3a** are in agreement with those reported from X-ray data for benzo-TCNQ ($\alpha = 158.3^\circ$, $\gamma = 19.2^\circ$)¹⁷ since the packing forces tend to planarize the molecules in order to achieve the most compact crystal packing.

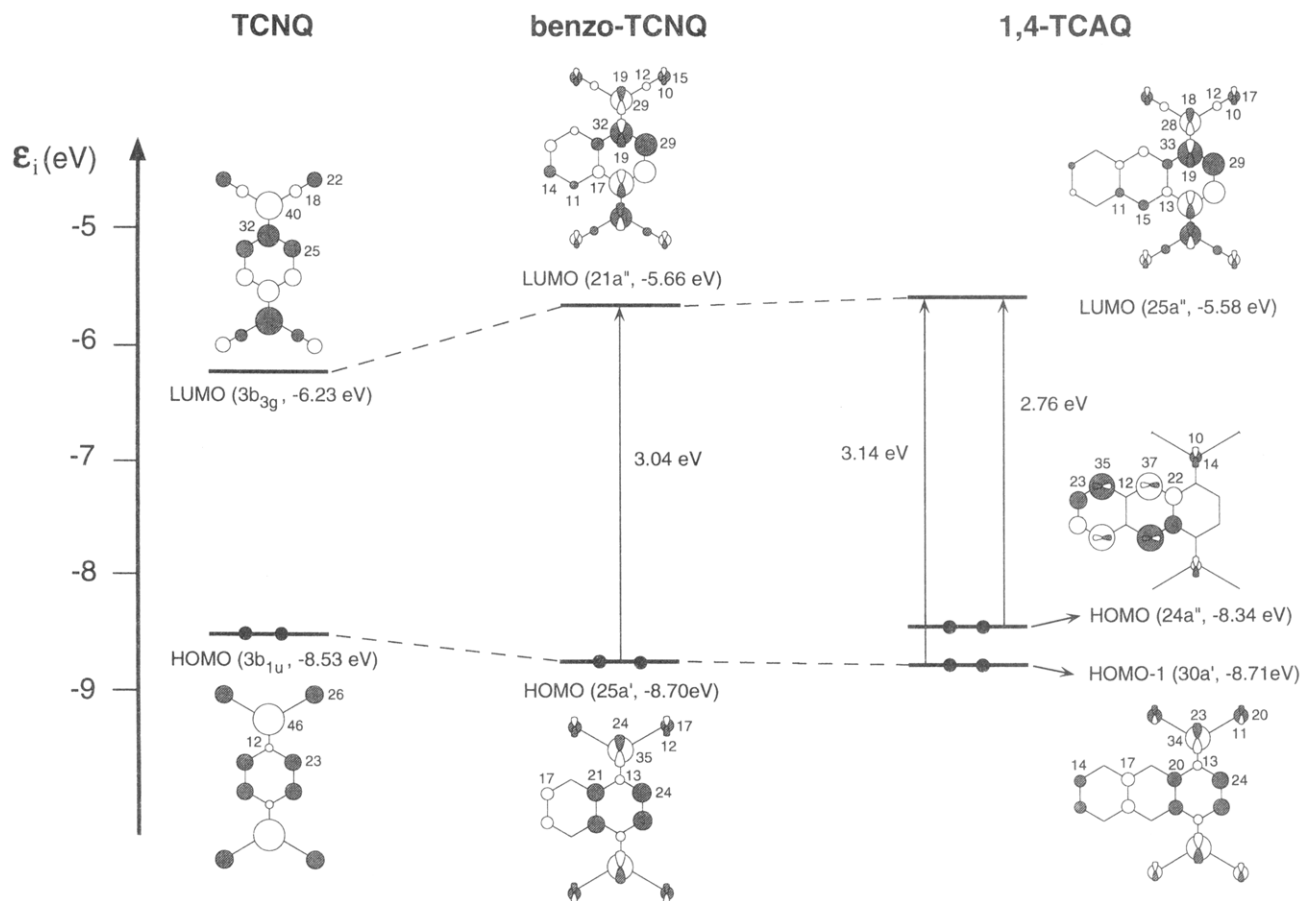


Figure 4. Molecular orbital diagram showing the energies, symmetries, and atomic orbital composition of the HOMO and LUMO of TCNQ (D_{2h} symmetry), benzo-TCNQ (C_s symmetry), and 1,4-TCAQ (C_s symmetry). The atomic orbital (AO) coefficients are given in units of 10^{-2} . Contributions from AOs other than π -type orbitals are due to the nonplanarity of the molecule.

The introduction of substituents in R1 and R2 positions causes a systematic increase of the distortion from planarity of 1,4-TCAQ due to the steric interaction of the substituents with the adjacent cyano groups. The attachment of one methoxy group (**3b**) slightly changes α and γ to 143.0° and 34.8° (28.8°), respectively. The presence of two additional methoxy groups on the lateral naphthalene unit (**3c**) affects these values by less than 0.1° . The introduction of two methyl groups (**3d**) or two chlorine atoms (**3e**) in R1 and R2 leads to a more important steric hindrance and the folding of the TCNQ ring is significantly larger for these compounds. In fact, the distortion from planarity of compound **3d** ($\alpha = 137.1^\circ$, $\gamma = 37.7^\circ$) is slightly more pronounced than that found for 9,10-TCAQ (**4**).

The PM3 method predicts that the benzoquinone ring in compounds **2** is slightly distorted from planarity. An angle α of 168.5° is, for instance, calculated for unsubstituted **2a**. Although nonplanar structures have been experimentally observed for hindered quinones,²⁵ the folding of the benzoquinone moiety in quinones **2** seems rather unlikely. We have therefore optimized the geometry of the closely related 1,4-naphthoquinone at the more accurate *ab initio* 6-31G* level. *Ab initio* calculations obtain a fully planar structure as the most stable conformation in accord with the X-ray data reported for 1,4-naphthoquinone.²⁶ It is thus shown that the nonpla-

nar structures predicted by the PM3 method for quinones **2** are an artifact of the method which provides too flat potentials for the bending of the quinone ring. The folded conformation in **2a** is indeed calculated to be more stable than the planar conformation by only 0.02 kcal/mol at the PM3 level.

Neutral Compounds: Electronic Structure. The electronic structure of 1,4-TCAQs was calculated using the PM3-optimized geometries and the nonempirical quantum-chemical VEH technique. Compared to standard *ab initio* Hartree-Fock calculations, the VEH method yields one-electron molecular orbital energies of double- ζ quality and has the advantage of providing good estimates for the lowest-energy optical transitions.^{27,28}

Figure 4 sketches the VEH atomic orbital composition of the highest occupied molecular orbitals (HOMO and HOMO-1) and the lowest unoccupied molecular orbital (LUMO) calculated for unsubstituted 1,4-TCAQ. These orbitals are correlated with those of the parent TCNQ and those of the less extended benzo-TCNQ. The LUMO of 1,4-TCAQ is spread over the TCNQ moiety and shows the same topology than the LUMOs of TCNQ and benzo-TCNQ. It has as energy of -5.58 eV and is destabilized with respect to TCNQ by 0.65 eV. This destabilization already appears for benzo-TCNQ (-5.66 eV) and is due to the lateral extension of the π -system that reduces the bonding interactions in the TCNQ ring and introduces

(24) Schubert, U.; Hünig, S.; Aumüller, A. *Liebigs Ann. Chem.* **1985**, 1216.

(25) Herbststein, F. H.; Kapon, M. *Acta Crystallogr. B* **1982**, 38, 3123.

(26) Gaultier, J.; Hauw, Ch. *Acta Crystallogr.* **1965**, 18, 179.

(27) Brédas, J. L.; Thémans, B.; André, J. M. *J. Chem. Phys.* **1983**, 70, 6137.

(28) Viruela-Martín, R.; Viruela-Martín, P. M.; Ortí, E. *J. Chem. Phys.* **1992**, 97, 8470.

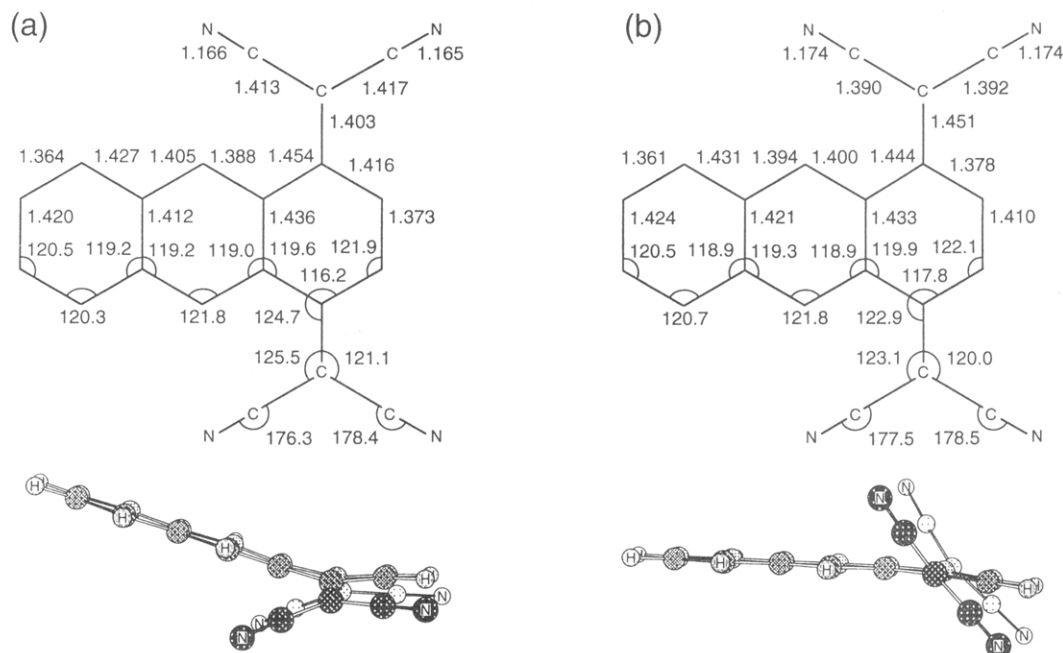


Figure 5. PM3-optimized geometries of the anion (a) and dianion (b) of nonsubstituted 1,4-TCAQ (**3a**). Bonds are in angstroms and angles in degrees. C_s symmetry is assumed.

new antibonding interactions. The LUMO of the closely related 9,10-TCAQ (-5.22 eV) is more destabilized because this molecule is more distorted from planarity and antibonding interactions are introduced on both sides of the TCNQ ring.

The HOMO of 1,4-TCAQ is located on the naphthalene moiety and does not correlate with the HOMOs of TCNQ and benzo-TCNQ. It is calculated at -8.34 eV and actually corresponds to the HOMO of the naphthalene molecule which has an energy of -8.49 eV. The HOMO of TCNQ is stabilized when the π -system is extended and for 1,4-TCNQ lies below the HOMO of naphthalene. It actually correlates with the HOMO-1 of 1,4-TCAQ.

The topologies of the HOMO and the LUMO of 1,4-TCAQ are also found for substituted 1,4-TCAQs (**3b–e**) and suggest that the HOMO \rightarrow LUMO electronic transition corresponds to an electron transfer from the naphthalene moiety, acting as a donor, to the acceptor TCNQ moiety. This electronic transition is calculated to appear at an energy of 2.76 eV (449 nm) for **3a** and of 3.17 eV (391 nm) for **3d** in quite good agreement with the lowest-energy absorption band observed experimentally for **3d** (442 nm), thus supporting the intramolecular charge-transfer nature of this band. Theoretical results therefore predict that the bathochromic shift observed here for the first optical absorption of 1,4-TCAQs ($\lambda_{\max} > 440$ nm) compared to 9,10-TCAQ ($\lambda_{\max} = 342$ nm)¹⁹ is not due to a larger delocalization of the π -system in 1,4-TCAQs, but to the appearance of an intramolecular charge-transfer absorption band at lower energies for 1,4-TCAQs. This band does not exist for the more symmetric 9,10-TCAQ because the lateral benzene moieties are not as good donors as the naphthalene unit present in 1,4-TCAQ. The charge-transfer nature of the longest wavelength band has also been suggested from theoretical calculations on the closely related TCPQ molecule²⁹ and from experimental data on the highly hindered 7,12-bis-

(dicyanomethylene)-7,12-dihydrobenz[*a*]anthracene.³⁰ In both cases, the naphthalene moieties preserve their structure and act as donors in the photoinduced charge transfer.

The HOMO \rightarrow LUMO electronic transition is calculated to appear at 3.04 eV (408 nm) for benzo-TCNQ in very good agreement with the lowest energy absorption band observed experimentally at 390 nm.^{19,31} For 1,4-TCAQs, this absorption band corresponds to the HOMO-1 \rightarrow LUMO electronic transition and is predicted to undergo a hypsochromic shift to higher energies. The value calculated for **3d** (3.33 eV, 372 nm) is in very good correlation with that observed experimentally (363 nm).

Reduced Compounds. The molecular structures of the anions and dianions of compounds **2** and **3** were optimized using the PM3 method in order to rationalize the electrochemical behavior of these compounds. Figure 5 shows the minimum energy geometries obtained for the anion and dianion of **3a**. The reduction process mainly affects the TCNQ moiety because the LUMO, i.e., the orbital where the extra electrons are placed, is located in this moiety as depicted in Figure 4. The introduction of the first electron to form the anion reduces the distortions from planarity of the TCNQ moiety. For **3a**, angle α increases to 162.0° and angle γ decreases to 15.0° compared with the values of 147.3° and 28.1° obtained for the respective angles in the neutral molecule. These changes are accompanied by a reduction of the quinoid character of the TCNQ ring. The C1–C2 and C3–C4 single bonds are shortened and the C2–C3, C1–C15, and C4–C20 bonds are lengthened.

The introduction of the second electron to form the dianion completes the aromatization process of the TCNQ moiety. Now, the TCNQ ring is approximately planar and forms an anthracene unit with the lateral naphthalene structure. The planarization process is made possible by the lengthening of the C1–C15 and C4–C20

(29) Viruela, R.; Viruela, P. M.; Ortí, E.; Martín, N. *Synth. Met.* **1995**, *70*, 1031.

(30) Maruyama, K.; Imahori, H.; Nakagawa, K.; Tanaka, N. *Bull. Chem. Soc. Jpn.* **1989**, *62*, 1626.

(31) Chatterjee, S. *J. Chem. Soc. B* **1967**, 1170.

bonds linking the dicyanomethylene groups to the aromatic unit which have a marked single bond character for the dianion (1.451 Å). The steric interactions between the cyano groups and the CH units in *peri* positions are therefore more readily alleviated by twisting the dicyanomethylene groups out of the aromatic plane rather than by folding the TCNQ ring. PM3 calculations predict that the C(CN)₂ groups are twisted by 43.8° with respect to the molecular plane in the dianion of **3a**. The lengthening of the C=C(CN)₂ double bonds and the twisting of the C(CN)₂ groups predicted for the dianion have been experimentally observed for perfluorinated and iodine disubstituted TCNQs in the charge-transfer salts {[Fe(C₅Me₅)₂]⁺}[TCNQF₄]²⁻ and {[Co(C₅Me₅)₂]⁺}[TCNQI₂]²⁻.^{32,33} For these compounds, the C(CN)₂ groups are found to be rotated out of the plane of the TCNQ ring by angles of 33° and 26°, respectively. The length of the C=C(CN)₂ double bonds in [TCNQF₄]²⁻ is 1.457 Å³² in accord with the value calculated for these bonds in **3a**.

Similar trends are obtained for substituted 1,4-TCAQs **3b** to **3e**. Table 2 collects the values of angles α and γ for the anions of these compounds. It should be noted that the most hindered derivatives, i.e., compounds **3d** and **3e**, remain highly distorted from planarity after accepting the first electron. The anion of the dimethyl derivative **3d** presents a distortion ($\alpha = 147.5^\circ$, $\gamma = 27.3^\circ$) similar to that shown by neutral 1,4-TCAQ ($\alpha = 147.3^\circ$, $\gamma = 28.1^\circ$). On the contrary, the anion of the less hindered methoxy derivative **3b** exhibits a distortion ($\alpha = 157.3^\circ$, $\gamma = 20.1^\circ$) similar to the anion of 1,4-TCAQ ($\alpha = 162.0^\circ$, $\gamma = 15.0^\circ$).

These structural differences explain the different electrochemical behavior exhibited by 1,4-TCAQ derivatives. The methoxy derivatives **3b** and **3c** undergo two one-electron reduction processes to the respective anion and dianion. The first reduction potential of these derivatives (~ -0.12 V) is considerably higher than that of the parent TCNQ (0.19 V) because the LUMO of 1,4-TCAQs is destabilized with respect to the LUMO of TCNQ (see Figure 4) due to the lack of planarity in the former. Furthermore, the resulting anions of 1,4-TCAQs are less aromatic than the anion of TCNQ because they are still distorted from planarity. This justifies the low stability found in Table 1 for the anions of **3b** and **3c** ($\log K \sim 3.2$) compared with that of the anion of TCNQ ($\log K = 9.65$). The second reduction potentials of **3b** and **3c** (~ -0.30 V) are almost identical to that of TCNQ (-0.36 V) because the dianions of **3b** and **3c** are completely planar and present an aromaticity similar to that of TCNQ²⁻. In the case of the more hindered **3d** and **3e** 1,4-TCAQ derivatives, the anion is more unstable because it is highly distorted from planarity and the dianion is planar and aromatic. This determines that the first reduction potential would appear at more negative values while the second reduction potential would remain unaffected. As a result, the reduction waves associated to the first and second reduction processes of **3d** and **3e** coalesce under one wave. This coalescence is also observed for 9,10-TCAQ²¹ and other π -extended TCNQ derivatives^{12,13} which present important distortions from planarity in both the neutral and anion states.

By contrast to the TCNQ derivatives, the anions and

dianions of quinones **2** are planar. This justifies the higher stabilities found for the anions of quinones (see Table 1) and the fact that quinones present differences between the first and second reduction potentials ($\Delta E \sim 0.5\text{--}0.6$ V) similar to that of TCNQ ($\Delta E = 0.55$ V).

Summary and Conclusions

The synthesis of the 1,4-TCAQs (**3**) has been carried out from the corresponding quinones **2** by using the Lehnert's reagent, thus proving the utility of this procedure to obtain different substitution degrees on the quinone ring. 1,4-TCAQs present a low-energy absorption band in the blue part of the visible region that is ascribed to an intramolecular charge-transfer band and is responsible of the red color that 1,4-TCAQs show. Cyclic voltammetry measurements reveal that these compounds exhibit a good acceptor ability and can be considered as precursors for organic metals. Their reduction provides stable radical anions and dianions or leads to the dianion in a two-electron wave depending upon the substitution pattern.

Molecular orbital calculations have been performed for the understanding of the experimental results. Semiempirical PM3 calculations show that 1,4-TCAQs are distorted from planarity and adopt a butterfly-type structure in which the TCNQ ring and the C(CN)₂ units are folded in opposite directions. The degree of distortion from planarity depends on the substitution pattern. The tetrasubstituted TCNQs with two methyl groups or two chlorine atoms attached to the TCNQ ring have the largest distortions, the folding of the TCNQ ring being similar to that reported for the closely related 9,10-TCAQ. PM3 calculations also show that the structural identity of naphthalene is preserved in 1,4-TCAQs.

The electronic structure of 1,4-TCAQs has been investigated using the nonempirical VEH method. This method predicts that the HOMO has no correspondence in TCNQ and is furnished by the lateral naphthalene unit, while the LUMO clearly correlates with the LUMO of TCNQ. The HOMO \rightarrow LUMO transition therefore corresponds to an electronic transition from the naphthalene unit, acting as a donor, to the acceptor TCNQ moiety. This result supports the intramolecular charge-transfer nature of the lowest-energy absorption band observed experimentally.

The molecular structures of the anions and dianions of 1,4-TCAQs have been optimized using the PM3 method. Since the LUMO is mainly located on the TCNQ acceptor moiety, this moiety is aromatized upon reduction. The anions are calculated to preserve some degree of nonplanarity specially in the case of the most hindered **3d** and **3e** derivatives. The dianions are predicted to be planar with the C(CN)₂ groups rotated out of the molecular plane. The nonplanarity of the anions justifies their low stability and explains the coalescence of the first and second reduction potentials for **3d** and **3e**.

Experimental Section

Computational Method. The equilibrium geometries of quinones **2** and 1,4-TCAQs **3** were calculated by means of the MNDO-PM3 (modified neglect of diatomic overlap, parametric method number 3) semiempirical method³⁴ as implemented in

(32) Dixon, D. A.; Calabrese, J. C.; Miller, J. S. *J. Phys. Chem.* **1989**, *93*, 2284.

(33) Miller, J. S.; Calabrese, J. C.; Harlow, R. L.; Dixon, D. A.; Zhang, J. H.; Reiff, W. M.; Chittipeddi, S.; Selover, M. A.; Epstein, A. J. *J. Am. Chem. Soc.* **1990**, *112*, 5496.

(34) Stewart, J. J. P. *J. Comput. Chem.* **1989**, *10*, 209. *Ibid.* **1989**, *10*, 221.

the MOPAC-6.0 system of programs.³⁵ The MNDO-PM3 method corresponds to a reparametrization of the MNDO approach³⁶ in which the AM1 (Austin model 1) form of the core-core interactions is used.³⁷ The suitability of the PM3 method to obtain reliable geometry estimates for organic compounds has been previously established.³⁵ With respect to MNDO, the PM3 technique provides a much improved description of the interactions taking place between nonbonded atoms, e.g., hydrogen bonding or steric interactions. The latter are specially important for the set of molecules studied in this work since they determine the planarity or nonplanarity of the system.

The geometry of neutral molecules and dianions were optimized within the restricted Hartree-Fock (RHF) formalism, while the spin-unrestricted Hartree-Fock (UHF)³⁸ approximation where electrons with different spins occupy different sets of orbitals was used for single-charged cations and anions. In all the calculations, the gradient norm achieved was less than 0.05.

The electronic structure of compounds **2** and **3** was investigated using the nonempirical valence effective Hamiltonian (VEH) pseudopotential technique.³⁹ This technique takes only into account the valence electrons and is based on the use of an effective Fock Hamiltonian where all the parameters used to build up the atomic potentials are optimized to reproduce the results of *ab initio* Hartree-Fock calculations. The VEH method is thus completely nonempirical since no experimental data enter the effective Fock Hamiltonian. It constitutes an especially useful tool to deal with large molecular systems, since it yields one-electron energies of *ab initio* double- ζ quality without performing any self-consistent-field (SCF) process or calculating any bielectronic integral. All the VEH calculations were performed using the atomic potentials previously optimized for hydrogen, carbon, and nitrogen atoms.⁴⁰ The validity of the VEH approach to study the electronic structure of large π -electronic molecular systems has been widely illustrated in previous works.^{41,42} The molecular geometry of 1,4-naphthoquinone was optimized at the *ab initio* level using the 6-31G* basis set⁴³ and the GAUSSIAN 92 program.⁴⁴

11,11,12,12-Tetracyano-1,4-anthraquinodimethanes (1,4-TCAQs) 3. *General Procedure.* To a solution of 1.0 mmol of the corresponding 1,4-anthracenedione **2**¹⁸ at room temperature in dry methylene dichloride or chloroform were added malononitrile (2.5 mmol) and then titanium tetrachloride (2.5

mmol) in dry pyridine (5 mmol) dropwise under argon atmosphere. After stirring at room temperature or reflux for 24 h the solvent was eliminated under vacuum and the solid obtained submitted to flash chromatography in florisil using hexane-ethyl acetate as the eluent. For compounds **3d** and **3e** an additional amount of malononitrile (2.5 mmol) and titanium tetrachloride (2.5 mmol) in pyridine (5 mmol) was added and the mixture refluxed for another 24 h. After cooling, the reaction mixture was filtered off, and the mother liquors were evaporated to dryness. Further purification was accomplished by recrystallization from acetonitrile.

11,11,12,12-Tetracyano-1,4-anthraquinodimethane (3a).¹⁴ This compound was obtained by following the above general procedure in 58% yield of crude compound.

11,11,12,12-Tetracyano-2-methoxy-1,4-anthraquinodimethane (3b). This compound was obtained by following the above general procedure in CH₂Cl₂ at room temperature for 24 h in 70% yield. M.p. 266–267 °C; ¹H NMR (CDCl₃; 300 MHz) δ 9.21 (H, s), 8.97 (H, s), 8.15–8.17 (2H, m), 7.78–7.80 (2H, m), 6.71 (H, s) and 4.13 (3H, s); IR (KBr) 3050, 2900–2850, 2220, 1600, 1530, 1520, 1480, 1280, and 1230 cm⁻¹; UV-vis (CHCl₃) λ_{\max} 491, 405, 313, 254. Anal. Calcd for C₂₁H₁₀N₄O: C, 75.44; H, 3.01; N, 16.76. Found: C, 75.70; H, 3.15; N, 16.90.

11,11,12,12-Tetracyano-2,6,7-trimethoxy-1,4-anthraquinodimethane (3c). This compound was obtained in CH₂Cl₂ at room temperature for 24 h in 63% yield. M.p. 270–272 °C; ¹H NMR (CDCl₃; 300 MHz) δ 8.98 (H, s), 8.71 (H, s), 7.15–7.8 (2H, m), 6.6 (H, s) and 3.98–3.94 (9H, 2s); IR (KBr) 3050, 2950, 2218, 1620, 1520, 1490, 1420, 1270, 1240, 1150, and 1000 cm⁻¹; UV-vis (CHCl₃) λ_{\max} 501, 419, 360, 266, 241. Anal. Calcd for C₂₃H₁₄N₄O₃: C, 70.05; H: 3.55; N: 14.21. Found: C, 70.28; H, 3.59; N, 14.20.

11,11,12,12-Tetracyano-2,3-dimethyl-1,4-anthraquinodimethane (3d). This compound was obtained in CH₂Cl₂ at reflux temperature for 48 h in 34% yield. Mp 284–286 °C; ¹H NMR (CDCl₃; 300 MHz) δ 8.63 (2H, s), 8.00 (2H, q), 7.75 (2H, q), 2.50 (6H, s); IR (KBr) 2240, 1545, 1530, 1500, 1450, 1400, 1390, 1360, 1300, 1185, 910, 900, and 770 cm⁻¹; UV-vis (CHCl₃) λ_{\max} 442, 363, 317, 260, 228; MS *m/e* 332 (M⁺, 100), 305 (20), 278 (10), 265 (12). Anal. Calcd for C₂₂H₁₂N₄: C, 79.50; H, 3.64; N, 16.86. Found: C, 79.64; H, 3.66; N, 17.08.

2,3-Dichloro-11,11,12,12-tetracyano-1,4-anthraquinodimethane (3e). This compound was obtained in CHCl₃ at reflux temperature for 48 h in 22% yield. Mp 240–242 °C; ¹H NMR (CDCl₃; 300 MHz) δ 8.78 (2H, s), 8.08 (2H, q) and 7.83 (2H, q); IR (KBr) 2920, 2230, 1550, 1520, 1290, and 780 cm⁻¹. Anal. Calcd for C₂₀H₆N₄Cl₂: C, 64.34; H, 1.61; N, 15.0. Found: C, 64.20; H, 1.50; N, 14.87.

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JO950227Q

(35) Stewart, J. J. P. MOPAC: A General Molecular Orbital Package (Version 6.0). *QCPE* 1990, 10, 455.

(36) Dewar, M. J. S.; Thiel, W. *J. Am. Chem. Soc.* 1977, 99, 4899.

(37) Dewar, M. J. S.; Zoebisch, E. G.; Healy, E. F.; Stewart, J. J. P. *J. Am. Chem. Soc.* 1985, 107, 3902.

(38) Pople, J. A.; Nesbet, R. K. *J. Chem. Phys.* 1954, 22, 571.

(39) Nicolas, G.; Durand, Ph. *J. Chem. Phys.* 1979, 70, 2020. *Ibid.* 1980, 72, 453. André, J. M.; Burke, L. A.; Delhalle, J.; Nicolas, G.; Durand, Ph. *Int. J. Quantum Chem. Symp.* 1979, 13, 283. Brédas, J. L.; Chance, R. R.; Silbey, R.; Nicolas, G.; Durand, Ph. *J. Chem. Phys.* 1981, 75, 255.

(40) André, J. M.; Brédas, J. L.; Delhalle, J.; Vanderveken, D. J.; Vercauteren, D. P.; Fripiat, J. G. In *Modern Techniques in Computational Chemistry: MOTTECC-90*; Clementi, E., Ed.; Escom: Leiden, The Netherlands, 1990; p 745. Brédas, J. L.; Thémans, B.; André, J. M. *J. Chem. Phys.* 1983, 78, 6137.

(41) Ortí, E.; Brédas, J. L. *J. Chem. Phys.* 1988, 89, 1009. Ortí, E.; Brédas, J. L. *J. Chem. Phys. Lett.* 1989, 164, 247. Ortí, E.; Brédas, J. L.; Clarisse, C. *J. Chem. Phys.* 1990, 92, 1228. Ortí, E.; Piqueras, M. C.; Crespo, R.; Brédas, J. L. *J. Chem. Mat.* 1990, 2, 110.

(42) Viruela-Martín, R.; Viruela-Martín, P. M.; Ortí, E. *J. Chem. Phys.* 1992, 96, 4474.

(43) Hariharan, P. C.; Pople, J. A. *J. Chem. Phys. Lett.* 1972, 16, 217.

(44) Frisch, M. J.; Trucks, G. W.; Head-Gordon, M.; Gill, P. M. W.; Wong, M. W.; Foresman, J. B.; Johnson, B. G.; Schlegel, H. B.; Robb, M. A.; Repogle, E. S.; Gomperts, R.; Anches, J. L.; Raghavachari, K.; Binkley, J. S.; González, C.; Martin, R. L.; Fox, D. J.; DeFrees, D. J.; Baker, J.; Stewart, J. J. P.; Pople, J. A. *Gaussian 92*; Gaussian: Pittsburgh, PA, 1992.