Molecular Saddles, 2[‡]

2,6-Dialkoxy-9,10-bis(1,3-dithiol-2-ylidene)-9,10-dihydroanthracene Derivatives: Synthesis, Electrochemistry and X-ray Crystal Structures of Neutral and Dication Species

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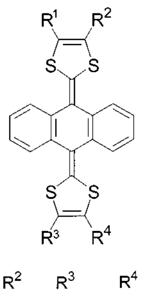
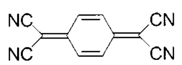
Keywords:

The synthesis of 2,6-dialkoxy-9,10-bis(1,3-dithiol-2-ylidene)-9,10-dihydroanthracene derivatives **15** and **16** is described. Solution electrochemistry shows that **15** and **16** display three redox waves, representing the sequential formation of the dication, radical trication and tetracation species in an $E_qE_qE_q$ process. The X-ray crystal structures of neutral compounds **15** and **16** and the charge transfer complex $(\mathbf{15})^{2+}(\mathrm{TCNQ}^{-\bullet})_2\cdot$2MeCN are reported. The neutral molecules adopt a saddle-like conformation; the bis(1,3-dithiole)benzoquinone system is U-shaped through an 'accumulating bend' comprising the boat conformation of the central (quinonoid) ring and folding of both 1,3-dithiole rings. In the complex $(\mathbf{15})^{2+}(\mathrm{TCNQ}^{-\bullet})_2\cdot$2MeCN the anthracene system is planar and aromatic; the dithiolium cations form a dihedral angle of 78° with the anthracene plane. The TCNQ anion radicals form a stack of dimers with interplanar separations of 3.15 Å within a dimer and 3.50 Å between the dimers. The structure contains unusually short intermolecular S···N contacts [2.865(3) Å].

Introduction

Following the pioneering studies of Hünig et al. on multistage redox systems,[1] bis(1,3-dithiole) derivatives with extended π-conjugation between the dithiole rings continue to attract attention as components of charge-transfer materials, some of which are electronic conductors.[2] Derivatives which have been widely studied include those with vinylogous conjugation and those with quinonoid or heteroaromatic spacer units. From this viewpoint, we have focused on 9,10-bis(1,3-dithiol-2-ylidene)-9,10-dihydroanthracene **1**,[3] and derivatives such as **2**–**6**.[3c–3e] The first derivative of this system, *viz*. 9,10-bis(benzo-1,3-dithiol-2-ylidene)-9,10-dihydroanthracene, was synthesised by Akiba et al.[4] A notable feature of compounds **1**–**6** is that they are strong π-electron donors undergo a single, two-electron, quasi-reversible oxidation wave to yield a thermodynamically stable dication at E^{ox} ca. +0.3 to +0.45 V (*vs* Ag/AgCl) in the cyclic voltammogram, with electron-withdrawing and electron-donating substituents on the dithiole rings shifting this wave to more positive and more negative potentials, respectively.[3c,5] We first reported that this π-donor system forms charge-transfer salts with TCNQ (TCNQ = 7,7,8,8-tetracyano-*p*-quinodimethane, **8**) and obtained X-ray crystal structures of the neutral system **2** and its dication salt $(\mathbf{2})^{2+}(\mathrm{TCNQ}_4)^{2-\bullet}$.[6] Subsequently, Triki et al. reported that derivative **7** interacts very differently with TCNQ **8** to form an unusual complex of formula $(\mathbf{7})^{2+}\mathrm{TCNQ}^0(\mathbf{9})_2{}^{2-}\cdot\mathrm{H_2O}$.[7] The formation of the rare oxidised TCNQ derivative **9** is thought to proceed *via* reaction of oxygen with the transient TCNQ^{2-} dianion.[8] It was clearly of interest to study new derivatives of system **1** and their complexes with TCNQ. Herein we report a new pattern of substitution, namely the attachment of flexible dialkoxy chains to the anthracene spacer. These chains serve to increase the solubility of the system in a range of organic solvents, compared to **1** and **2**, thereby facilitating electrochemical and complexation studies. We describe the synthesis of derivatives **15** and **16**, their solution electrochemistry and the X-ray crystal structures of both neutral species **15** and **16** and the TCNQ salt $(\mathbf{15})^{2+}(\mathrm{TCNQ}^{-\bullet})_2\cdot$2MeCN.





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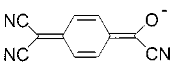

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	R^1	R^2	R^3	R^4
1	H	H	H	H
2	Me	Me	Me	Me
3	SMe	SMe	SMe	SMe
4	Me	Me	Me	CO_2Me
5	Me	Me	Me	SMe
6	Me	Me	SEt	SEt
7	Me	SMe	SMe	Me

[‡] Part 1: Ref.[3e]

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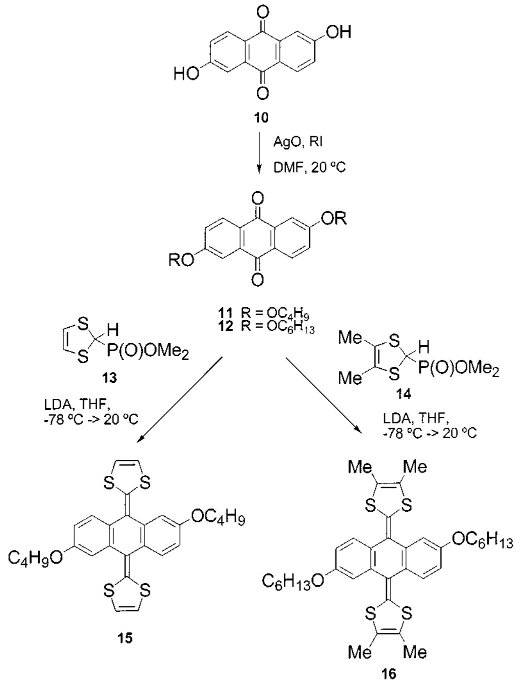
Results and Discussion

Synthesis

2,6-Dihydroxyanthraquinone (**10**) was readily converted into the dialkoxy derivatives **11** and **12** [silver(I) oxide, 1-iodobutane or 1-iodohexane, in *N*,*N*-dimethylformamide] which subsequently underwent two-fold Horner–Wadsworth–Emmons reactions with the phosphonate anion obtained by deprotonation of reagents **13**[3c] and **14**[3c] (lithium diisopropylamide in THF at –78 °C) respectively, to yield compounds **15** and **16** (51–59% yields) (Scheme 1). A crystalline complex of **15** and TCNQ of stoichiometry (**15**)$^{2+}$(TCNQ$^{-\bullet}$)$_2$·2MeCN was obtained from an acetonitrile solution of the two components, and the stoichiometry deduced from the X-ray crystal structure.



Scheme 1. Synthesis of compounds **15** and **16**

Solution Electrochemistry of 15 and 16

The solution electrochemistry of compounds **15** and **16** has been studied by cyclic voltammetry (CV) and by square wave voltammetry (SQV) in acetonitrile. Both compounds display three redox waves at the following potentials: compound **15** E^{ox} 0.330, 1.49 and 1.64 V; compound **16** E^{ox} 0.275, 1.47 and 1.62 V. The lower values of these potentials for the latter compound, especially E_1^{ox}, is consistent with the trend observed with compounds **1** and **2**, arising from tetramethyl substitution on the 1,3-dithiole rings.[3c] Analysis of the data is consistent with an $E_\mathrm{q}E_\mathrm{q}E_\mathrm{q}$ process (E_q = quasi-reversible). Figure 1 shows the SQV for compound **15**. The first wave is a two-electron process (neutral → dication, with aromaticity gain at the dication stage) and the second, one-electron wave is ascribed to oxidation of the anthracene unit (dication → radical trication) by analogy with previous work.[5,9] Repeated recycling through the first wave resulted in no significant change in the CV, demonstrating that this is a chemically reversible redox process. The effect of the alkoxy substituents is to shift the second oxidation wave to lower potentials by ca. 150 mV (*cf.* compounds **1** E_2^{ox} 1.64, and **2** E_2^{ox} 1.62 V, under the same conditions). The entirely new feature of compounds **15** and **16** is the presence of a third redox wave, which is also a quasi-reversible, one-electron process. This wave has not been unambiguously observed in previous derivatives of system **1**, (it was very tentatively seen for the 2,3-dipentylanthracene analogue of **2** at ca. + 2.2 V, i.e. at the limit of the solvent window)[5a] and we assign this process to the formation of the tetracation species **15**$^{4+}$ and **16**$^{4+}$ which could be stabilised by the electron-donating effect of the two alkoxy substituents.[10] This assignment is further supported by comparison with the voltammetric data for 9,10-diphenylanthracene[11] which undergoes two, single-electron, oxidation waves (E_1^{ox} 1.23, and E_2^{ox} 1.69 V, vs. SCE in MeCN)[11a] and these waves (especially E_2^{ox}) are cathodically shifted in 9,10-bis(*p*-methoxyphenyl)anthracene (E_1^{ox} 1.15, and E_2^{ox} 1.37 V). This latter separation (ΔE^{ox} 220 mV) approaches the value (ΔE^{ox} 150 mV) which we observe for E_2^{ox} and E_3^{ox} for compounds **15** and **16**. We eliminated the possibility that this third wave for **15** and **16** was derived from a different chemical species (*eg* a species in which the alkoxy groups had been cleaved in the electrochemical reaction) as recycling between 1.00 and 1.75 V for 50 cycles resulted in no significant change in the appearance of the CV.

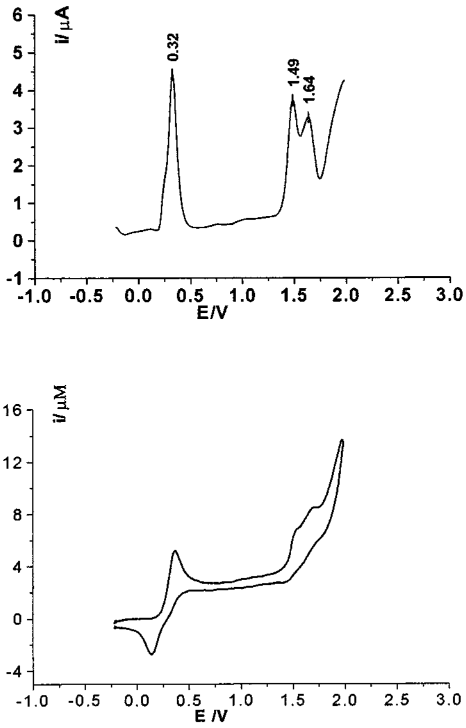


Figure 1. Electrochemistry of compound **15**; (top) square wave voltammogram; (bottom) equivalent cyclic voltammogram

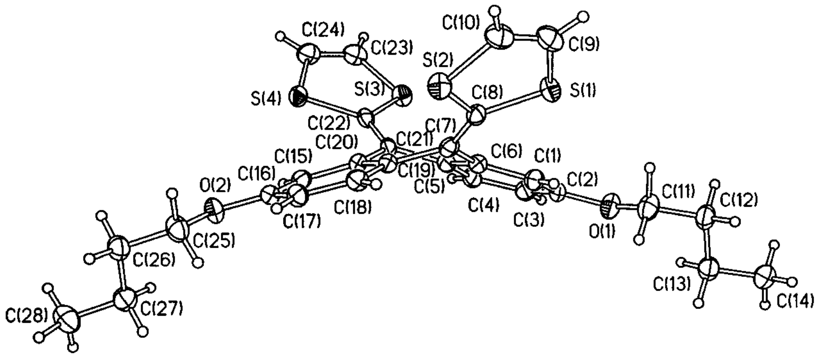


Figure 2. Molecular structure of **15**, showing 50% displacement ellipsoids

X-ray Crystal Structures of 15, 16 and $(15)^{2+}(TCNQ^{-\bullet})_2 \cdot 2MeCN$

Neutral molecule **15** (Figure 2) adopts a saddle-like conformation, similar to the previously reported analogues **2**–**6** with various substituents at the dithiole carbon atoms.[3d,3e,6] The anthracene system is folded along the C(7)···C(21) vector by 34.6° (*cf.* 38–45° in **2**–**6**) and actually comprises two isolated benzene π-systems, linked to C(7) and C(21) by single bonds. The bis(dithiole)benzoquinone system displays an 'accumulating bend' inward, with a dihedral angle of 91.5° between the S(1)C(9)C(10)S(2) and S(3)C(23)C(24)S(4) planes (*cf* 76–87° in **2**–**6**). Both 1,3-dithiole rings are folded along the S(1)···S(2) and S(3)···S(4) vectors by 6.6 and 10.0°, respectively. The crystal packing motif is the usual one of dimers, wherein the U-shaped bis(dithiole)benzoquinone systems engulf each other.

The molecular structure of **16** (Figure 3) is similar to that of **15**. Folding of the anthracene moiety in **16** (44.8° along the C(7)···C(25) vector) is stronger, but folding of the dithiole rings [5.9° and 12.2° along the S(1)···S(2) and S(3)···S(4) vectors, respectively] and the overall U-bend of the bis(dithiole)benzoquinone system, measured by the dihedral angle between the S(1)C(9)C(10)S(2) and S(3)C(27)C(28)S(4) moieties (90.0°) are practically the same in the two structures. It is evident that a nonplanar molecular conformation is, in principle, necessary to distance sulfur atoms from the *peri* hydrogens of the anthracene moiety (in agreement with theoretical calculations[5b]). However, this nonplanarity is achieved by a number of modes of distortion, which show no obvious correlation with each other or with electronic properties of the substituents. Thus the actual degree of bending is rather flexible and can adjust to the demands of crystal packing.

The asymmetric unit of $(\mathbf{15})^{2+}(TCNQ^{-\bullet})_2.2MeCN$ comprises a TCNQ anion radical and an acetonitrile molecule in general positions, and half of a $(\mathbf{15})^{2+}$ dication, located at a crystallographic inversion centre (Figure 4). The dication has the structure similar to that in $(\mathbf{2})^{2+}(TCNQ_4)^{2-\bullet}$ [6] and in $(\mathbf{7})^{2+}TCNQ^0(\mathbf{9})_2{}^{2-}\cdot H_2O$.[7] The anthracene system is planar and aromatic; the bond lengths therein (Table 1) are essentially the same as in neutral anthracene.[12] The dithiolium rings are also planar; their geometry is close to that in $(TMTTF)(ClO_4)_2$ [13] and is consistent with the charge of *ca* +1 on each ring. The dithiolium cations and anthracene planes form a dihedral angle of 78°; the intervening C(7)–C(8) bond is essentially single. It is well-known[14] that charge transfer onto a TCNQ molecule results in lengthening of the C=C bonds *p* and *r* (Scheme 2) and shortening of the single bonds *q* and *s*, so that $q \approx r \approx s$ for the charge of –1. In $(\mathbf{15})^{2+}(TCNQ^{-\bullet})_2 \cdot 2MeCN$, the average

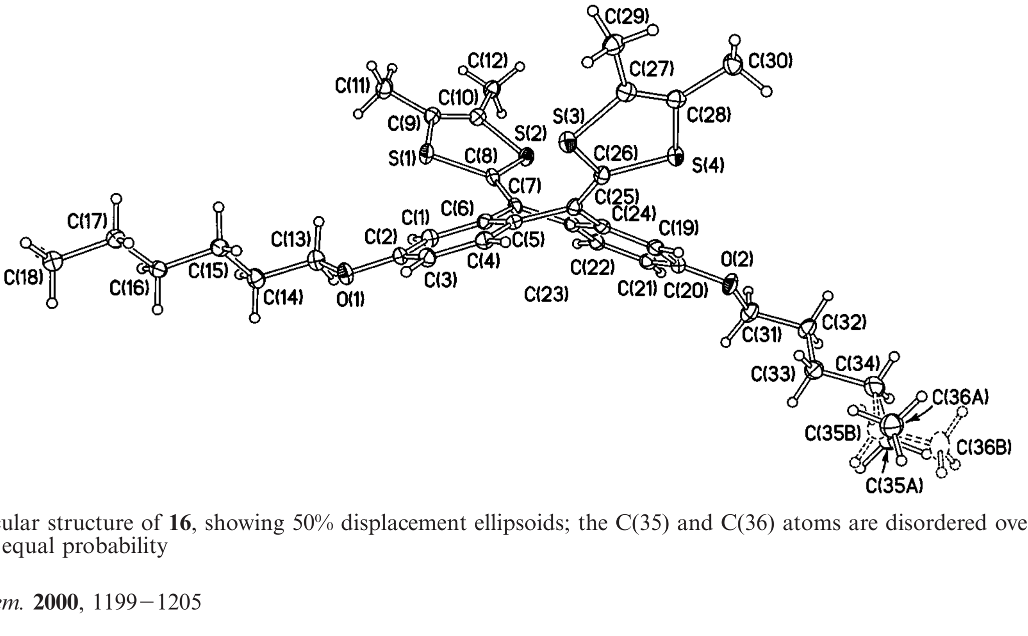


Figure 3. Molecular structure of **16**, showing 50% displacement ellipsoids; the C(35) and C(36) atoms are disordered over two positions (A and B) with equal probability

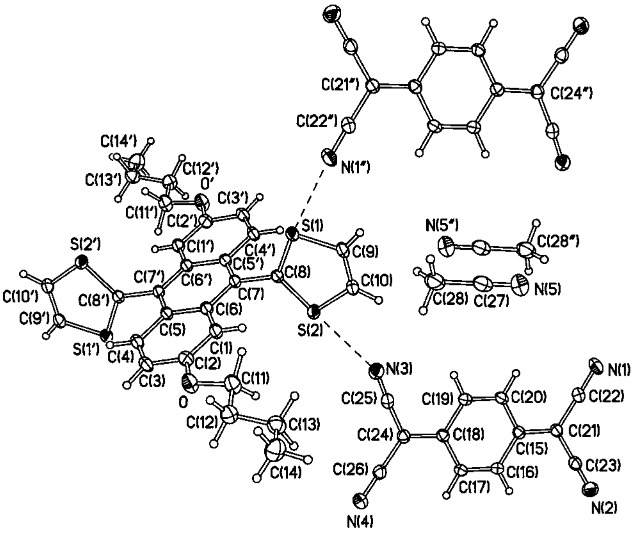
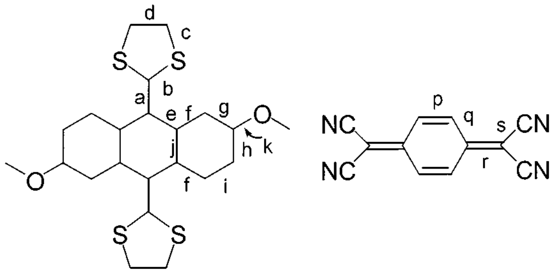


Figure 4. Formula unit of $(\mathbf{15})^{2+}(\mathrm{TCNQ}^{-\bullet})_2\cdot 2\mathrm{MeCN}$ in crystal, showing 50% displacement ellipsoids. Primed atoms are symmetrically related via inversion centres

Table 1. Average bond lengths in **15**, **16** and $(\mathbf{15})^{2+}(\mathrm{TCNQ}^{-\bullet})_2\cdot 2\mathrm{MeCN}$ (Å).

Bond	15	16	$(\mathbf{15})(\mathrm{TCNQ})_2\cdot 2\mathrm{MeCN}$
a	1.366(3)	1.365(3)	1.486(2)
b	1.770(3)	1.769(2)	1.680(2)
c	1.745(3)	1.767(2)	1.710(2)
d	1.319(4)	1.333(3)	1.346(3)
e	1.477(3)	1.483(3)	1.413(2)
f	1.400(3)	1.397(3)	1.436(2)
g	1.395(3)	1.394(3)	1.375(2)
h	1.391(3)	1.392(3)	1.428(2)
i	1.385(3)	1.390(3)	1.356(3)
j	1.417(3)	1.421(3)	1.440(2)
k	1.364(3)	1.374(2)	1.357(2)



Scheme 2. Identification of bonds for crystallographic analysis (see Table 1)

distances $p = 1.371(2)$, $q = 1.425(2)$, $r = 1.423(2)$ and $s = 1.423(2)$ Å clearly indicate TCNQ to be a mono anion radical. (The nitrile stretching frequencies in the IR spectra at 2172 and 2155 cm^{-1}, support this.) Selected bond lengths are collated in Table 1.

Crystallographically parallel anion radicals form a stack of dimers (Figure 5) with interplanar separations of 3.15 Å within a dimer and 3.50 Å between dimers. The anions in a dimer overlap with a slip (from the eclipsed position) of ca. 0.8 Å in the direction perpendicular to the C(21)···C(24) vector. According to MO calculations,[15] the energy minimum of a $(\mathrm{TCNQ})_2^{2-}$ dimer corresponds to a slip of 2.1 Å *along* this vector. Indeed, the latter (ring-over-bond) mode of overlap is usually observed in crystal structures of TCNQ salts, including that of $(\mathbf{2})^{2+}(\mathrm{TCNQ}_4)^{2-\bullet}$.[6] Within the dimer, the C···C contacts are in the range of 3.24 to 3.33 Å (*cf.* normal van der Waals contact[16] of 3.59 Å) indicating strong coupling between the anion radicals. On the other hand, all the inter-dimer C···C contacts are ≥3.56 Å. In contrast, the structure of $(\mathbf{2})(\mathrm{TCNQ})_4$ contains continuous stacks of TCNQ with a uniform interplanar spacing of 3.36 Å.[6]

The anthracene moieties of the $(\mathbf{15})^{2+}$ cations also form a stair-like stack, but perpendicular orientation of the dithiolium rings enforces a large interplanar separation of 3.97 Å, while leading to rather short intercation contacts S(1)···C(3) 3.289(2) Å (*cf.* normal contact 3.61 Å[16]). A notable feature of the structure is that both sulfur atoms of the dithiolium ring participate in short contacts with nitrogen atoms of the TCNQ: S(1)···N(1″)(–*x*, 1–*y*, –*z*) 2.959(3) and S(2)···N(3) 2.865(3) Å, *cf.* the standard van der Waals contact of 3.42 Å.[16] In either case, the contacting nitrogen atom is nearly co-planar with the dithiolium ring and opposite to the C(8)–S bond, *viz*. the angles C(8)–S(1)–N(1) 173.1(2)° and C(8)–S(2)–N(3) 178.5(2)°. Short contacts of this kind are rather common in charge transfer complexes comprising TCNQ and TTF or their derivatives and could be expected, since the N and S atoms are the main centres of negative and positive charges, respectively. Thus, the celebrated organic metal TTF·TCNQ[17] contains S···N contacts of 3.17 Å. Nevertheless, the shortest S···N distance observed in such systems (3.04 Å)[18] is still much longer than in the present structure. The difference can be attributed to the fact, that in $(\mathbf{15})^{2+}$ each dithiolium ring has twice the positive charge than in $\mathrm{TTF}^{+\bullet}$. However, in similarly charged $(\mathbf{2})^{2+}(\mathrm{TCNQ}_4)^{2-\bullet}$ [6] and $(\mathbf{7})^{2+}(\mathrm{TCNQ})^0(\mathbf{9})_2^{2-}\cdot\mathrm{H_2O}$[7] salts, the closest S···N contacts are significantly longer: 3.07 and 3.14 Å, respectively. Therefore, in the salt $(\mathbf{15})^{2+}(\mathrm{TCNQ}^{-\bullet})\cdot 2\mathrm{MeCN}$ one can suppose some degree of hypervalent S···N interaction. A few D-π-A molecules studied earlier[2d,19] had similar *intra*molecular S···N contacts (2.68–2.73 Å) between the π-donor (dithiole) and π-acceptor $[\mathrm{C(CN)_2}$ or NCN] parts of the molecule.

Conclusions

We have synthesised new derivatives of 9,10-bis(1,3-dithiol-2-ylidene)-9,10-dihydroanthracene possessing flexible dialkoxy substituents. Cyclic voltammetric data establish increased π−donor strength with the detection of the tetracation oxidation state. X-ray crystal structures reveal the dramatic conformational change which accompanies oxidation of the neutral molecule **15** to the dication. The complex $(\mathbf{15})^{2+}(\mathrm{TCNQ}^{-\bullet})_2.2\mathrm{MeCN}$ is the third TCNQ complex of a 9,10-bis(1,3-dithiol-2-ylidene)-9,10-dihydroanthracene donor to be characterised crystallographically. Its stoichiometry is different from that of its two predecessors; a not-

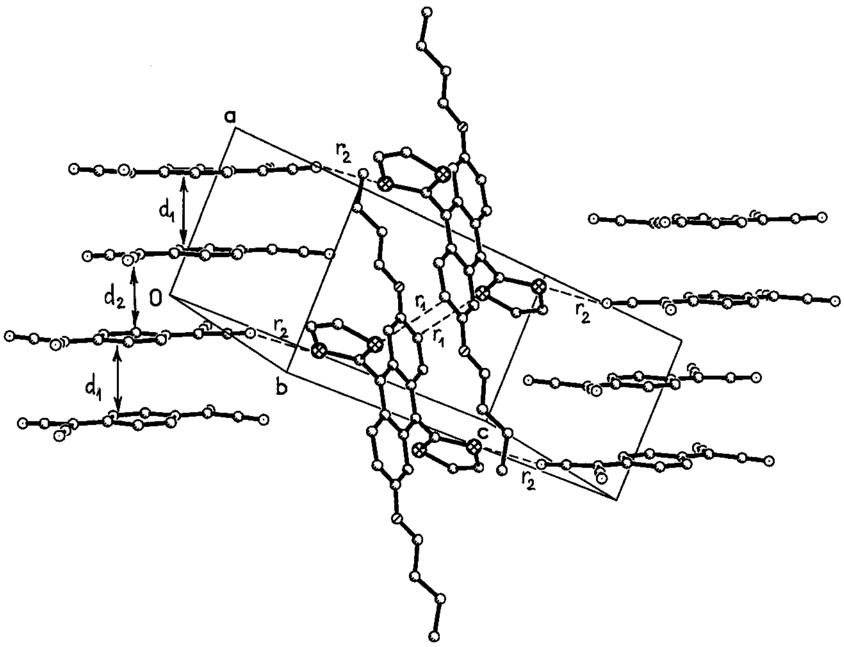


Figure 5. Crystal packing of $(\mathbf{15})^{2+}(\mathrm{TCNQ}^{-\bullet})_2 \cdot 2\mathrm{MeCN}$ (acetonitrile molecules and all H atoms are omitted). Interplanar separations $d_1 = 3.15$, $d_2 = 3.50$ Å, C···S contacts $r_1 = 3.289(2)$ Å, N···S contacts $r_2 = 2.865(3)$ Å

able feature of the structure is that both sulfur atoms of the dithiolium ring participate in short intermolecular contacts with nitrogen atoms of a TCNQ moiety. This study further demonstrates that 9,10-bis(1,3-dithiol-2-ylidene)-9,10-dihydroanthracene is a very interesting π-electron rich system, the unusual redox and structural properties of which should stimulate studies on new derivatives.

Experimental Section

General: ^{1}H and ^{13}C NMR Spectra were obtained on Oxford 200, Varian Unity 300 and Varian VXR 400S spectrometers operating at 199.992 (^{1}H) and 50.293 (^{13}C), 299.908 (^{1}H) and 75.420 (^{13}C), and 400.0 (^{1}H) and 100.6 (^{13}C) MHz, respectively. − Mass spectra were recorded on a Micromass Autospec spectrometer operating at 70 eV. – Elemental analyses were obtained on an Exeter Anaytical Inc. CE-440 Elemental Analyzer. – Melting points were obtained on a Philip Harris melting point apparatus and are uncorrected. – All reagents were of commercial quality; solvents were dried using standard procedures. – All reactions were performed under an inert atmosphere of argon in pre-dried glassware. – Cyclic voltammetric and square wave data were measured with iR compensation using an EGG 263 potentiostat. The experiments were carried out with 5 mL of a ca. 10^{-4} M solution of the compound in acetonitrile containing 0.1 M tetrabutylammonium hexafluorophosphate (Fluka, puriss, electrochemical grade) as the supporting electrolyte, at scan rate 100 mV s^{-1}. The oxidation potentials (which represent a two-electron process) were measured *versus* a platinum wire auxiliary electrode and corrected *versus* decamethylferrocene/decamethylferrocenium$^+$ by adding decamethylferrocene to the studied solution after the experiment, and referenced *versus* Ag/AgCl.[20] – The data were analysed using EG and G PARC′s model 271 COOL Kinetic Analysis Software (V 1.2.3). The voltammograms were analysed in separate sections, and 95% confidence limits were achieved.

2,6-Dibutyloxyanthraquinone (11): To a solution of 2,6-dihydroxyanthraquinone (**10**) (0.487 g, 1.15 mmol) in dry *N,N*-dimethylformamide (100 mL) at 20 °C was added silver(I) oxide (0.981 g mg, 4.23 mmol) and 1-iodobutane (0.7 mL, 6.15 mmol) immediately. The mixture was stirred for 48 h under an argon atmosphere, then the solvent was removed in vacuo. The residue was purified by column chromatography on silica gel with acetone/hexane (1:3) as the eluent to afford **11** (205 mg, 56%) as a yellow solid. M.p. 109–111 °C. – ^{1}H NMR (CDCl$_3$): δ = 1.00 (t, 6 H, J = 7 Hz), 1.55 (m, 4 H), 1.84 (m, 4 H), 4.15 (t, 4 H, J = 7 Hz), 7.26 (m, 2 H), 7.69 (s, 2 H), 8.19 (d, 2 H, J = 9 Hz). – ^{13}C NMR (CDCl$_3$): δ = 13.7, 19.1, 31.0, 68.4, 110.4, 120.8, 126.9, 129.5, 135.7, 163.9, 182.2. – MS (CI); *m/z* (%): 353 (100) [M$^+$ + 1]. – $C_{22}H_{24}O_4$ (352.4): calcd. C 75.0, H 6.9; found C 74.7, H, 6.9.

2,6-Dihexyloxyanthraquinone (12): Following the same procedure as for compound **11**, 2,6-dihydroxyanthraquinone (2.45 g, 10.2 mmol) in dry dimethylformamide (250 mL), silver(I) oxide (9.69 g, 41.8 mmol) and 1-iodohexane (6 mL, 41 mmol) afforded **12** (2.31 g, 57%) as a yellow solid. M.p. 90–92 °C. – ^{1}H NMR (CDCl$_3$): δ = 0.91 (t, 6 H, J = 7 Hz), 1.36 (m, 8 H), 1.49 (m, 4 H), 1.83 (p, 4 H, J = 7 Hz), 4.12 (t, 4 H, J = 7 Hz), 7.19 (dd, 2 H, J_{ab} = 2 Hz, J_{bc} = 9 Hz), 7.67 (d, 2 H, J_{bc} = 2 Hz), 8.20 (d, 2 H, J_{ab} = 9 Hz). – ^{13}C NMR (CDCl$_3$): δ = 14.0, 22.6, 25.6, 29.0, 31.5, 68.8, 110.5, 120.8, 126.9, 129.6, 135.8, 164.0, 182.2. – MS (CI); *m/z* (%): 409 (100) [M$^+$ + 1] – $C_{26}H_{32}O_4$ (408.5): calcd. C 76.4, H 7.9; found C 76.0, H, 7.9.

2,6-Dibutyloxy-9,10-bis(1,3-dithiol-2-ylidene)-9,10-dihydroanthracene (15): Into a solution of 2-dimethoxyphosphinyl-1,3-dithiole (**13**)[3c] (1.0 g, 4.71 mmol) in dry tetrahydrofuran (50 mL) at −78 °C, was added lithium diisopropylamide (3.6 mL of 1.5 M solution in cyclohexane, 5.4 mmol) over a period of 15 min. The reaction mixture was left for 3 h until a pale cloudy solution formed. Then a solution of compound **11** (508 mg, 1.44 mmol) in dry tetrahydrofuran (10 mL) was added over 15 min. The reaction was stirred overnight at 20 °C. The reaction mixture was evaporated in vacuo, and the residue was purified by column chromatography on

Table 2. Crystal data

Compound	**15**	(**15**)(TCNQ)$_2$·2MeCN	**16**
Formula	$C_{28}H_{28}O_2S_4$	$C_{28}H_{28}O_2S_4^{2+}\cdot(C_{12}H_4N_4^{-})_2\cdot 2C_2H_3N$	$C_{36}H_{44}O_2S_4$
Mol. mass	524.74	1015.24	636.95
T [K]	150	120	120
Crystal dimensions [mm]	0.40 × 0.30 × 0.15	0.8 × 0.4 × 0.4	0.30 × 0.15 × 0.07
Crystal system	monoclinic	triclinic	triclinic
Space group	$P2_1/c$ (No. 14)	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)
a [Å]	11.506(1)	7.105(1)	10.414(1)
b [Å]	17.027(1)	9.884(1)	11.447(1)
c [Å]	13.254(1)	17.937(1)	15.159(5)
α [°]	90	92.46(3)	92.09(1)
β [°]	103.28(1)	93.75(3)	103.87(1)
γ [°]	90	91.40(2)	112.43(1)
U [Å^3]	2527.1(4)	1255.3(4)	1605.1(6)
Z	4	1	2
λ [Å]	1.54184	0.71073	0.71073
μ [mm^{-1}]	3.64	0.24	0.33
D_x [g cm^{-3}]	1.379	1.343	1.318
$2\varphi_{max}$/°	150	55	55
No. of refl. collected	5801	14201	12690
No. of unique refl.	4845	5721	7261
No. of refl. with $I \geq 2\sigma(I)$	4020	5111	5008
Transmission min, max	0.758, 1	-	0.917, 0.979
No. of variable params.	419	409	498
$R[I \geq 2\sigma(I)]$	0.043	0.041	0.042
Goodness of fit	1.06	1.03	1.00
$wR(F^2)$, all data	0.114	0.113	0.097
$\Delta\rho_{max,min}$ [eÅ^{-3}]	0.44, –0.35	0.41, –0.29	0.35, –0.31

silica gel with hexane/dichloromethane (2:1 v/v) as eluent to afford **15** a yellow solid (260 mg, 51%). M.p. 129–133 °C. Crystals were grown from acetonitrile. – ^{1}H NMR (CDCl$_3$): δ = 0.98 (t, 6 H, J = 7 Hz), 1.50 (m, 4 H), 1.80 (m, 4 H), 4.03 (t, 4 H, J = 7 Hz), 6.23 (s, 4 H), 6.80 (dd, 2 H, J_{ab} = 3, J_{bc} = 9 Hz), 7.26 (d, 2 H, J_{bc} = 3 Hz), 7.50 (d, 2 H, J_{ab} = 9 Hz). – ^{13}C NMR (CDCl$_3$): δ = 13.8, 19.4, 31.2, 31.0, 31.3, 67.9, 68.5, 110.5, 110.9, 111.9, 117.1, 120.9, 122.2, 126.0, 126.9, 128.2, 129.6, 133.4, 135.8, 136.9, 157.1, 164.0, 182.3. – MS (DCI); m/z (%): 524 (100) [M$^+$]. – $C_{28}H_{28}O_2S_4$ (524.7) calcd. C 64.1, H 5.3; found C 63.7, H 5.3.

2,6-Dihexyloxy-9,10-bis(4,5-dimethyl-1,3-dithiol-2-ylidene)-9,10-dihydroanthracene (16): Following the procedure for compound **15**, 2-dimethoxyphosphinyl-4,5-dimethyl-1,3-dithiole **14**[3c] (129 mg, 0.538 mmol) in dry tetrahydrofuran (50 mL), lithium diisopropylamide (0.4 mL of 1.5 M solution in cyclohexane, 0.59 mmol) and a solution of compound **12** (97 mg, 0.24 mmol) in dry tetrahydrofuran (5 mL) afforded **16** a yellow oil which solidified on standing (92 mg, 59%). M.p. 123–125 °C. Crystals were grown from deuteriochloroform. – ^{1}H NMR (CDCl$_3$): δ = 0.92 (m, 6 H), 1.37 (m, 12 H), 1.82 (m, 4 H), 1.92 (s, 12 H), 4.03 (t, 4 H, J = 6.6 Hz), 6.78 (dd, 2 H J = 2.6 and 8.6 Hz), 7.14 (d, 2 H, J = 2.6 Hz), 7.51 (d, 2 H, J = 8.6 Hz). – ^{13}C NMR (CDCl$_3$): δ = 13.1, 14.1, 22.6, 25.7, 29.2, 31.6, 68.2, 105.4, 111.3, 111.6, 120.7, 121.4, 126.3, 128.1, 130.9, 136.8, 156.9. – MS (DCI); m/z (%): 636 (100) [M$^+$]. – $C_{36}H_{44}S_4O_2$ (637.0) calcd. C 67.9, H 7.0; found C 67.6 H, 7.0 .

Complex (15)$^{2+}$(TCNQ$^{-\bullet}$)$_2$·2MeCN: Equimolar solutions of **15** and TCNQ (**8**) in hot dry acetonitrile were mixed. The solution was cooled to room temperature, and slow partial evaporation afforded black crystals of the complex (**15**)$^{2+}$(TCNQ$^{-\bullet}$)$_2$·2MeCN suitable for X-ray analysis. – IR: $\tilde{\nu}_{max}$ (golden gate) = 2360, 2344, 2172, 2155, 1559, 1496 cm^{-1}.

X-ray Crystallography: For **15**, single-crystal X-ray diffraction data were collected on a Rigaku AFC6S 4-circle diffractometer (graphite-monochromated Cu-K_α radiation, $2\varphi/\omega$ scan mode) and processed using TEXSAN[21] software, with an empirical absorption correction[22] based on 108 ψ-scans of 3 reflections. For **16** and (**15**)$^{2+}$(TCNQ$^{-\bullet}$)$_2$·2MeCN the diffraction experiments were performed with a SMART 1 K CCD area detector mounted on a 3-circle diffractometer (graphite-monochromated Mo-K_α radiation). Four sets of ω scans (each set at different ϕ and/or 2θ angles) nominally covered over a hemisphere of reciprocal space. Reflection intensities were integrated using SAINT[23] software and (for **16**) corrected for absorption by numerical integration technique based on crystal dimensions (8 faces indexed, SHELXTL software[24]). The crystals were maintained at low temperature with Cryostream (Oxford Cryosystems) open-flow N$_2$ gas cryostats. All the structures were solved by direct methods and refined by full-matrix least squares against F^2 of all data, using SHELXTL software.[24] Non-H atoms were refined in anisotropic, and H atoms in isotropic approximation. Crystal data and experimental details are listed in Table 2. Reference numbers CCDC-135059, –135060 and –135061 for compounds **15**, (**15**)$^{2+}$(TCNQ$^{-\bullet}$)$_2$·2MeCN and **16**, respectively.

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[1] [1a] K. Deuchert, S. Hünig, *Angew. Chem. Int. Ed. Engl.* **1978**, *17*, 875–886. – [1b] S. Hünig, H. Berneth, *Top. Cur. Chem.* **1980**, *92*, 1–44.

[2] [2a] Z. Yoshida, T. Sugimoto, *Angew. Chem. Int. Ed. Engl.* **1988**, *27*, 1573−1157. – [2b] T. Sugimoto, H. Awaji, I. Sugimoto, Y. Misaki, T. Kawase, S. Yoneda, Z. Yoshida, *Chem. Mater.* **1989**, *1*, 535−547. – [2c] M. R. Bryce, A. J. Moore, B. K. Tanner, R. Whitehead, W. Clegg, F. Gerson, A. Lamprecht, S. Pfenninger, *Chem. Mater.* **1996**, *8*, 1182−1188. – [2d] A. J. Moore, M. R. Bryce, A. S. Batsanov, A. Green, J. A. K. Howard, M. A. McKervey, P. McGuigan, I. Ledoux, E. Ortí, R. Viruela, P. M. Viruela, B. Tarbit, *J. Mater. Chem.* **1998**, *8*, 1173−1184. – [2e] Y. Yamashita, M. Tomura, M. B. Zaman, M. Imaeda, *Chem. Commun.* **1998**, 1657–1658. – [2f] Review: Y. Yamashita, M. To-

mura, *J. Mater. Chem.* **1998**, *8*, 1933−1944. – [2g] Review: J. Yamada, H. Nishikawa, K. Kikuchi, *J. Mater. Chem.* **1999**, *9*, 617–628.

[3] [3a] Y. Yamashita, Y. Kobayashi, T. Miyashi, *Angew. Chem. Int. Ed. Engl.* **1989**, *28*, 1052−1053. – [3b] M. R. Bryce, A. J. Moore, D. Lorcy, A. S. Dhindsa, A. Robert, *J. Chem. Soc., Chem. Commun.* **1990**, 470−472. – [3c] A. J. Moore, M. R. Bryce, *J. Chem. Soc., Perkin Trans. 1* **1991**, 157−168. – [3d] A. S. Batsanov, M. R. Bryce, M. A. Coffin, A. Green, R. E. Hester, J. A. K. Howard, I. K. Lednev, N. Martín, A. J. Moore, J. N. Moore, E. Ortí, L. Sánchez, M. Savíron, P. M. Viruela, R. Viruela, T-Q. Ye, *Chem. Eur. J.* **1998**, *4*, 2580−2592. – [3e] M. R. Bryce, T. Finn, A. J. Moore, A. S. Batsanov, J. A. K. Howard, *Eur. J. Org. Chem.* **2000**, 51−60.

[4] K. Akiba, K. Ishikawa, N. Inamoto, *Bull. Chem. Soc. Jpn.* **1978**, *51*, 2674−2683.

[5] [5a] M. R. Bryce, M. A. Coffin, M. B. Hursthouse, A. I. Karaulov, K. Müllen, H. Scheich, *Tetrahedron Lett.* **1991**, *32*, 6029−6033. – [5b] N. Martín, L. Sánchez, C. Seoane, E. Ortí, P. M. Viruela, R. Viruela, *J. Org. Chem.* **1998**, *63*, 1268−1279.

[6] M. R. Bryce, A. J. Moore, M. Hasan, G. J. Ashwell, A. T. Fraser, W. Clegg, M. B. Hursthouse, A. I. Karaulov, *Angew. Chem. Int. Ed. Engl.* **1990**, *29*, 1450−1452.

[7] S. Triki, L. Ouahab, D. Lorcy, A. Robert, *Acta Cryst.* **1993**, *C49*, 1189−1192.

[8] M. R. Suchanski, R. P. van Duyne, *J. Am. Chem. Soc.* **1976**, *98*, 250–251.

[9] For studies on the related 7-(1,3-dithiol-2-ylidene)-7-hydrobenz[d,e]anthracene system see: N. Martín, E. Ortí, C. Sánchez, P. M. Viruela and R. Viruela, *Eur. J. Org. Chem.* **1999**, 1239–1247.

[10] A lowering of the oxidation potentials (by 300–400 mV) of thianthrene derivatives by attachment of four alkoxy substituents has been noted previously: K.-W. Stender, G. Klar, *Z. Naturforsch* **1985**, *40b*, 774–781.

[11] [11a] O. Hammerich, V. D. Parker, *J. Am. Chem. Soc.* **1974**, *93*, 4289–4296. – [11b] J. O. Howell, R. M. Wrighton, *J. Phys. Chem.* **1984**, *88*, 3915–3918.

[12] C. Pratt Brock, J. D. Dunitz, *Acta Crystallogr. Sect. B* **1990**, *46,* 795–806.

[13] R. P. Shibaeva, *Kristallografiya* **1984**, *29*, 480–483.

[14] S. Flandrois, D. Chasseau, *Acta Crystallogr. Sect. B* **1977**, *33*, 2744–2750.

[15] J. P. Lowe, *J. Am. Chem. Soc.* **1980**, *102*, 1262–1269.

[16] R. S. Rowland, R. Taylor, *J. Phys. Chem.* **1996**, *100*, 7384–7391.

[17] A. J. Schultz, G. D. Stucky, R. H. Blessing, P. Coppens, *J. Am. Chem. Soc.* **1976**, *98*, 3194– 3201.

[18] F. Ivasaki, S. Hironaka, N. Yamazaki, K. Kobayashi, *Bull. Chem. Soc. Jpn.* **1992**, *65*, 2180– 2186.

[19] M. R. Bryce, M. A. Chalton, A. S. Batsanov, C. W. Lehmann, J. A. K. Howard, *J. Chem. Soc., Perkin Trans. 2* **1996**, 2367–2371.

[20] [20a] J. L. Robbins, N. Edelstein, B. Spenser, *J. Am. Chem. Soc.* **1982**, *104*, 1882–1893. – [20b]P. G. Gassman, D. W. Macomber, J. W. Hershberger, *Organometallics* **1983**, *2*, 1470–1472.

[21] *TEXSAN: Single crystal structure analysis software, Version 5.1*, Molecular structure corporation, Woodlands, Texas, USA, **1989**.

[22] A. C. T. North, D. C. Phillips, F. S. Mathews, *Acta Crystallogr. Sect. A* **1968**, *24*, 351– 359.

[23] *SMART and SAINT, Release 4.05, Area detector control and integration software.* Bruker Analytical X-ray Systems, Madison, Wisconsin, USA, **1995**.

[24] G. M. Sheldrick, *SHELXTL, version 5.10 DOS/WIN95/NT*, Bruker Analytical X-ray Systems, Madison, Wisconsin, USA, **1997**.

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