Perchlorophenalenyl Radical

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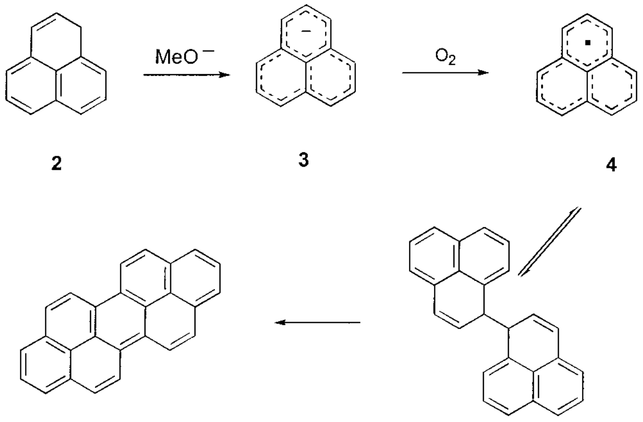
Received May 23, 2000

Abstract: We report the preparation and solid-state characterization of the perchlorophenalenyl radical (**1**). The radical is initially obtained as a yellow-green solid by reduction of the perchlorophenalenium salt ($\mathbf{12}^{+}$). This solid sublimes in a sealed tube to give black shiny hexagonal crystals of the perchlorophenalenyl radical (**1**). The structure consists of 1-dimensional stacks of the monomeric radical. The peri-chlorine atoms force the phenalenyl system to be strongly nonplanar leading to a large separation between adjacent molecules within the stacks (3.78 Å), and the molecules adopt two distinct stacking motifs (quasisuperimposed and rotated by 60° with respect to neighbors). Because of the packing frustration in the lattice and the large intermolecular spacing, the solid shows Curie paramagnetism in the temperature range 100−400 K, before antiferromagnetic coupling sets in at low temperatures. Due to the narrow bandwidth that results from the isolation of the individual molecules, the solid is a Mott−Hubbard insulator, with a room-temperature conductivity of $\rho_{\mathrm{RT}} = 10^{-10}$ S/cm.

Introduction

A number of years ago it was suggested that a crystal containing stacks of π-radicals [such as phenalenyl (**4**)] would give rise to highly conducting materials.[1−3] Since that time it has become apparent that such compounds are likely to suffer from a large on-site Coulomb correlation energy and are expected to exhibit electronic instabilities that lead to insulating ground states. Recently our group has attempted to design molecules that circumvent some of these problems while retaining the attractive features of the neutral radical approach to organic conductors.[4,5] Nevertheless, we felt that it was of interest to devise a π-radical that conformed to the original thesis.[1] The primary problem in attempting to test this idea is associated with the propensity of these systems to undergo σ-dimerization, a difficulty that is known to occur with the parent phenalenyl system (**4**).

The phenalenyl radical (**4**) is green in the solid state and can be prepared from phenalene (**2**), as shown below.[6−8] The EPR spectrum of phenalenyl (**4**) has been measured, and this technique can be used to follow the σ-dimerization reaction.[9] Cooling a solution of **4** gives the diamagnetic dimer **5**, which on warming disassociates back to radical **4**,[10] indicating that the two compounds are in thermodynamic equilibrium. Dimer **5** disproportionates slowly at room temperature to afford peropyrene (**6**) and another unidentified hydroaromatic product.



2 **3** **4**

6 **5**

Thus σ-dimerization prevents the isolation of crystalline parent phenalenyl radical (**4**). This problem was partially overcome recently by the preparation of the 2,5,8-tri-*tert*-butylphenalenyl radical (**7**).[11] Phenalenyl **7** cannot undergo σ-dimerization as a result of the steric hindrance provided by the tertiary butyl groups. A single-crystal X-ray structure

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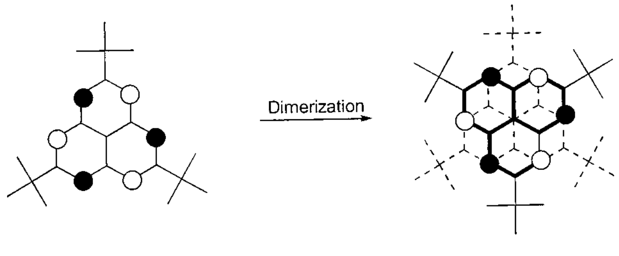
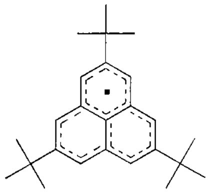


7a **7b**

Figure 1. Diagram of the solid-state structure of the 2,5,8-tri-*tert*-butylphenalenyl radical (**7**).[11] The molecules form discreet face-to-face π-dimers with C···C separations in the range 3.2–3.3 Å. One molecule of the dimer is rotated 60° with respect to the other (as found in the relationship between the superimposed trimers in the 1-dimensional stacks in **1**). The solid and open circles give the phase of the coefficients of the singly occupied nonbonding molecular orbital of the phenalenyl system.

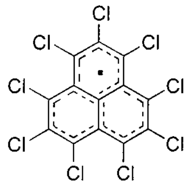
determination of solid state **7** showed that the phenalenyl ring system is slightly distorted from D_{3h} symmetry and has a nearly planar geometry with small deviations of the butyl groups from the plane of the ring. The molecules form discreet face-to-face π-dimers with C···C separations in the range 3.2–3.3 Å. One molecule of the dimer is rotated 60° with respect to the other to minimize the steric interaction of the tertiary butyl groups while maintaining almost perfect overlap of the α-carbon atoms (which carry most of the spin density as shown by the coefficients of the singly occupied nonbonding molecular orbital pictured in Figure 1). The dimers stack in a herringbone motif.



7

This system illustrates the subtle balance that must be struck with substituents that are employed to inhibit σ-dimerization. If the substituents are too bulky they can inhibit the communication that is necessary between molecules in the lattice that ultimately leads to conductivity. A good example is provided by perchlorotriphenylmethyl where the bulk of the substituents leads to very stable radicals that apparently do not interact with one another in the solid state.[12] Pentaisopropylcyclopentadienyl forms a stacked structure, but due to the alkyl groups the cyclopentadienyl rings are separated by 5.82 Å.[13]

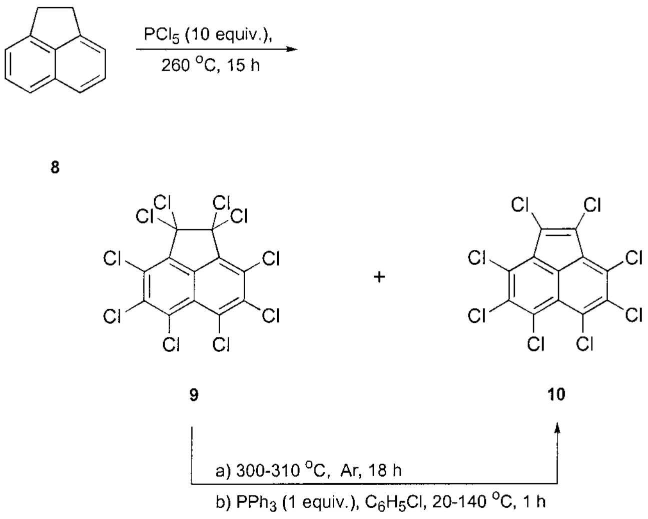
In the past we have employed both sulfur and chlorine as substituents to block dimerization (and delocalize the spin density), without inhibiting contact between neighboring π-systems.[14,15] However, we have hitherto been unable to crystallize these compounds even though we could detect them in solution by spectroscopic techniques. In the present study we report the complete preparative details for the perchlorophenalenyl radical (PCPLY, **1**), together with its solid-state properties.



1

Chemical Synthesis of Perchlorophenalenyl (1). Perchloroacenaphthylene (**10**) has been prepared by two techniques,[16–18] and we previously[15] made use of the powerful chlorinating agent known as BMC, a mixture of $AlCl_3$, S_2Cl_2, and SO_2Cl_2,[19] to synthesize **10**. BMC has been used to perchlorinate coronene (90% yield)[20] and corannulene (65% yield),[21] and to convert acenaphthylene into perchloroacenaphthene (**9**) (27% yield).[18] On melting (255–260 °C) perchloroacenaphthene (**9**) loses 1 equivalent of molecular chlorine to give **10**.[16]

Phosphorus pentachloride (PCl_5) has been used to perchlorinate pyridine[22] under moderate pressure and temperature in sealed reaction vessels. When we applied these reaction conditions to acenaphthene (**8**), we obtained a mixture of perchloroacenaphthene (**9**) and perchloroacenaphthylene (**10**). Compound **9** could be converted into perchloloacenaphthylene (**10**) either by thermolysis (300–310 °C) or on treatment with triphenylphosphine to afford a high recovery of **10** (84%). Dechlorination with triphenylphosphine was the preferred route for large-scale preparation of **10**.



In the original synthesis of perchloro-7*H*-cyclopropano[*a*]-acenaphthylene (**11**),[15] we added dichlorocarbene to perchloroacenaphthylene (**10**) by use of phenyl(bromodichloromethyl)-mercury (Seyferths reagent).[23] Even in the presence of a

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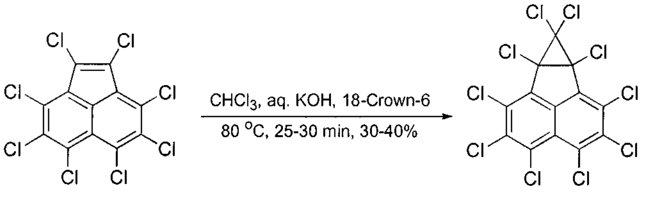
6-fold excess of the mercurial and with prolonged reaction times, only 50% of **10** underwent the cyclopropanation reaction, and the incomplete consumption of the starting material required chromatography of the reaction mixture on Florisil.[15]

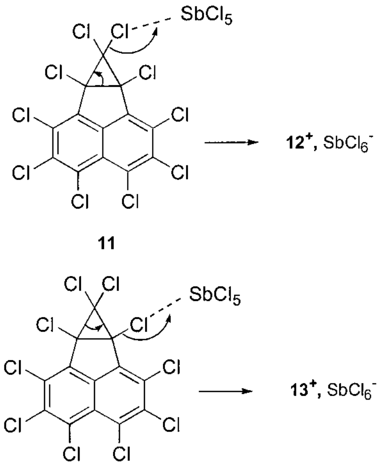
In the present work, we have employed the haloform reaction to prepare **11** using 18-crown-6 as phase transfer catalyst (PTC), even though the yield based on **10** is still in the range of 30−40%. This reaction has the advantage that it utilizes readily available reagents ($CHCl_3$, KOH, water, and crown ether) and very short reaction times (25 min) and does not require chromatography to recover the product.



10 **11**

Perchlorophenalenium hexachloroantimonate ($\mathbf{12}^+$, $SbCl_6^-$) was originally generated in situ by Lewis acid abstraction of chloride from **11** followed by a cyclopropyl to allyl rearrangement.[15] Such reagents gave deep red suspensions in a red solution and the color was taken to be indicative of the formation of the phenalenium cation. These reaction mixtures, presumably containing the cation ($\mathbf{12}^+$, $SbCl_6^-$), underwent reduction to give solutions of the perchlorophenalenyl radical **1**.

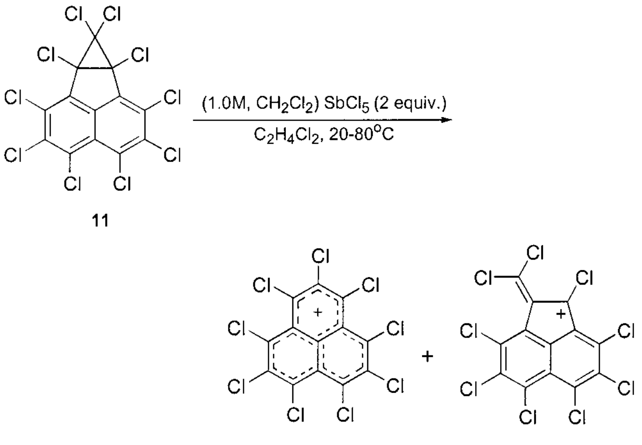
We have reinvestigated the reaction of $SbCl_5$ (1.0 M in CH_2Cl_2) with solutions of **11** in anhydrous 1,2-dichloroethane and found that the solid that is isolated by filtration under argon consists of a mixture of two isomeric salts in a combined yield of 81−88%. The major component of the precipitate is the desired perchlorophenalenium hexachloroantimonate ($\mathbf{12}^+$, $SbCl_6^-$), but it is accompanied by the allyl isomer ($\mathbf{13}^+$, $SbCl_6^-$). On the basis of this observation it seems likely that $SbCl_5$ is able to abstract chloride ion from either of the chloroalkane sites in **11**.



11

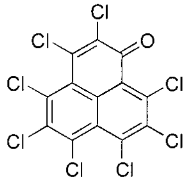
11

Hydrolysis of the filtrate from the $SbCl_5$ reaction gave four byproducts, isomer **14** and three carbonyl-containing compounds **15**, **16**, and phenalenone (**17**).



11

$\mathbf{12}^+$, $SbCl_6^-$ $\mathbf{13}^+$, $SbCl_6^-$



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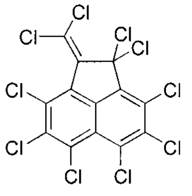

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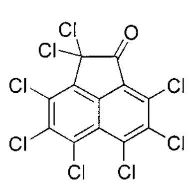

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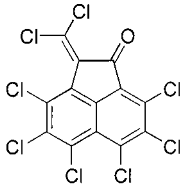

16

Compounds **16** and **17** presumably arise from simple hydrolysis of the salts $\mathbf{13}^+$, $SbCl_6^-$ and $\mathbf{12}^+$, $SbCl_6^-$, respectively. It seems likely that compound **14** arises from back transfer of chloride from the $SbCl_6^-$ anion to the salt **13**, and there is precedent for such transformations in the literature.[24−26] Formation of acenaphthylone (**15**), which is produced in the filtrate of the $SbCl_5$ reaction but not from the direct hydrolysis of the salts $\mathbf{12}^+$, $SbCl_6^-$ and $\mathbf{13}^+$, $SbCl_6^-$, presumably arises from the Lewis acid-catalyzed hydrolysis of compound **14**.

Fortunately, we found that the milder Lewis acid, gallium trichloride, abstracted chloride ion from cyclopropane (**11**), to afford exclusively perchlorophenalenium tetrachlorogallate ($\mathbf{12}^+$, $GaCl_4^-$). The gallium salt $\mathbf{12}^+$, $GaCl_4^-$ was obtained as bright green crystals with a lustrous golden shine. The salt was filtered under argon to give $\mathbf{12}^+$, $GaCl_4^-$ in good yield (87%). Hydrolysis of salt $\mathbf{12}^+$, $GaCl_4^-$ in wet acetone gave phenalenone (**17**) in a 79% yield; compounds **14**−**16** were not detected and this observation supports the absence of salt $\mathbf{13}^+$, $GaCl_4^-$ in the gallium trichloride reaction with **11**.

The perchlorophenalenyl radical (**1**) was previously detected in solution by EPR spectroscopy, on in situ reduction of $\mathbf{12}^+$, $SbCl_6^-$.[15] The large-scale availability of pure ($\mathbf{12}^+$, $GaCl_4^-$) has allowed us to the prepare and characterize samples of the radical **1** in gram quantities, by reduction of the gallium salt with stoichiometric quantities of reducing agents such as anhydrous

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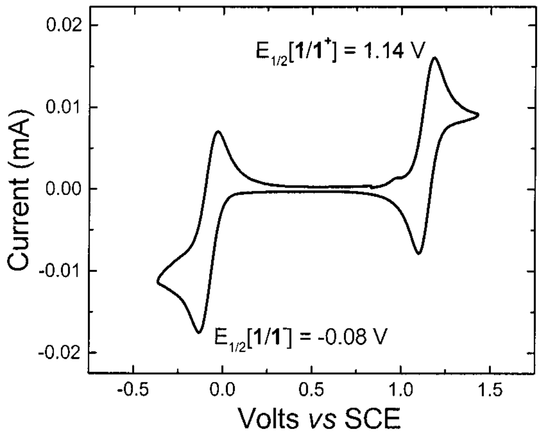
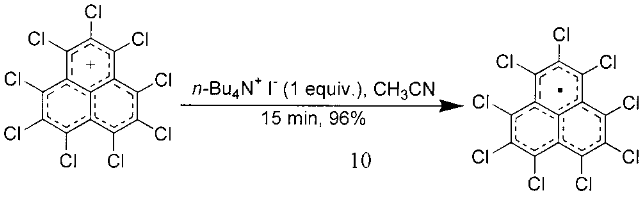


Figure 2. Cyclic voltammogram of PCPLY (**1**), in CH_2Cl_2, with 0.1 M Bu_4NPF_6 as supporting electrolyte.

n-tetrabutylammonium iodide.



12$^+$, $GaCl_4^-$ **1**

(10)

On reduction of **12**$^+$, $GaCl_4^-$, the crude perchlorophenalenyl radical (**1**) is formed rapidly as a bright yellow precipitate, which quickly turns olive green.

Radical **1** can be chromatographed (hexane) on silica in air as reported previously,[15] although a significant loss of material was observed. While the radical is relatively stable to oxygen, it will react to give perchlorophenalenone (**17**), together with other compounds. The major impurity in the crude radical (**1**) as prepared from purified salt **12**$^+$, $GaCl_4^-$ was perchlorophenalenone (**17**). Repeated sublimation along a glass tube in a 3-zone tube furnace under high vacuum (5×10^{-5} Torr) gave shiny black hexagonal columns [melting point, 160 °C with decomposition in air, 248 °C under argon]. IR analysis of the first sublimations indicated the black crystals were still contaminated with perchlorophenalenone (**17**); however, after four sublimations the black crystals showed no trace of the phenalenone (**17**) and gave a correct microanalysis for $C_{13}Cl_9$.

Electrochemistry of Perchlorophenalenyl (1). For purposes of consistency we have, in the past, performed all cyclic voltammetry measurements using CH_3CN as solvent, Bu_4NPF_6 as supporting electrolyte, and the Fc/Fc^+ couple as the quasireference electrode.[27] The low solubility of **1** in CH_3CN, however, prompted us initially to explore the use of CH_2Cl_2, in which the radical is considerably more soluble. The results are illustrated in Figure 2. Within the range −0.5 to 1.5 V vs SCE two reversible one-electron processes are observed, corresponding to the oxidation ($1/1^+$, $E_{1/2} = 1.14$ V) and reduction ($1/1^-$, $E_{1/2} = -0.08$ V) of perchlorophenalenyl (**1**). When performed in CH_3CN, the reduction wave remains reversible, and the half-wave potential $E_{1/2}$(red) is shifted to −0.025 V. However, the oxidation wave ($E_{pa} = 0.97$ V) is no longer reversible, and switching the supporting electrolyte (to Bu_4NClO_4) caused no change. We have no immediate explanation for the loss of reversibility of the oxidation process under these conditions. The electrochemistry of the parent phenalenyl system was also found to be irreversible in CH_3CN;[14] half-wave potentials of 0.7 ($E_{1/2}$, oxidation) and −0.9 V ($E_{1/2}$, reduction) were estimated for this radical.

It is useful to compare the CH_2Cl_2 and CH_3CN data for perchlorophenalenyl (**1**) with the results on dithiadiazolyl radicals, for which there is a relatively large body of electrochemical data from both solvent systems.[28,29] First, the relatively large (200 mV) cathodic shift of E_{pa} between CH_2Cl_2 (1.17 V) and CH_3CN (0.97 V) for **1** parallels that found for dithiadiazolyl radicals, which undergo a shift of similar magnitude and direction between CH_2Cl_2 and CH_3CN.[30] For the latter systems the $E_{1/2}$(red) value is generally insensitive to solvent change, and while there is a shift (of ca. 60 mV) in the present case, it is much smaller than that seen for the oxidation process. In summary, the redox potentials for perchlorophenalenyl and dithiadiazolyls exhibit the same solvent dependence, as a result of which $E_{1/2}$ values measured in CH_2Cl_2 are slightly larger than those taken from CH_3CN.

The electrochemical data provide a useful insight into the chemical properties of PCPLY (**1**). Most substituted phenalenyl derivatives are quite electropositive, and generation of the radicals from their respective cations requires relatively strong reducing agents (e.g., Cp_2Co).[5,14,31,32] By contrast, the perchlorinated periphery of **1** generates a very electronegative core, as a result of which perchlorophenalenyl becomes almost halogen-like in its redox behavior. Iodide ion is now sufficient to reduce the PCPLY cation to PCPLY which, in contrast to other phenalenyl radicals, is stable with respect to atmospheric oxidation. Similar behavior, as a function of substituent, has been noted for heterocyclic thiazyl radicals.[4]

Structure of Perchlorophenalenyl (1). Resublimation of the purified radical in a sealed tube that was heated in a 3-zone furnace gave large shiny black hexagonal columns that were suitable for single-crystal X-ray structure determination.

The radical crystallizes in a modulated superstructure that give rise to a number of refinement difficulties, and full details of the structural solution will appear shortly.[33] The individual molecules of perchlorophenalenyl (**1**, $C_{13}Cl_9$) are ruffled into a propeller shape (see Figure 3) because the Cl···Cl distances in a planar molecule would be impossibly short. The van der Waals radius of a Cl atom is 1.80 Å, but even after distortion, the three short intramolecular Cl···Cl distances at the peri-positions are only 3.02−3.03 Å. The same type of distortions from planarity have been observed in naphthalenes that are halogenated at the peri-positions.[34,35]

The molecules of **1** are stacked in columns, each of which has 3-fold rotational symmetry (Figure 4). Adjacent molecules within the stacks are arranged in quasisuperimposed trimers. Neighboring trimers are rotated by about 60° so as to minimize eclipsing interactions, as predicted on theoretical grounds[3] and seen in the structure of **7**.[11] The columns form an hexagonally close-packed array, and within each stack the intermolecular

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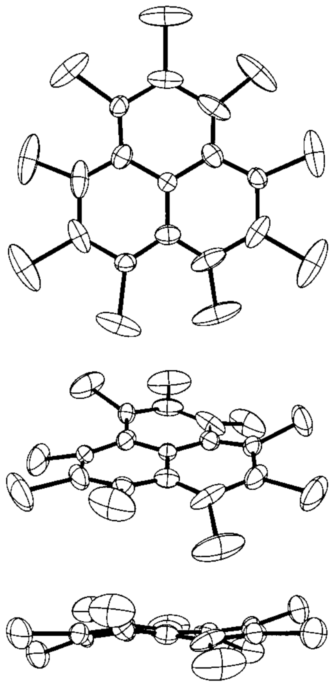


Figure 3. Views of the molecular structure of perchlorophenalenyl (**1**).

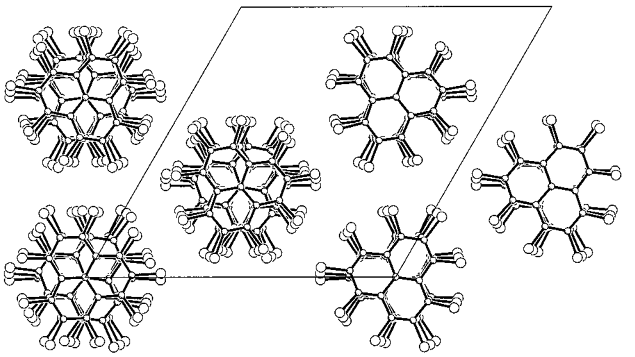
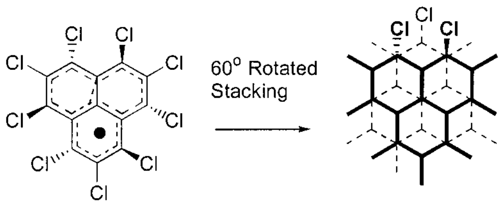


Figure 4. Projection down *c* of the $C_{13}Cl_9$ superstructure of (**1**). Two sets of the three independent stacks are shown. The set on the left shows all six molecular orientations for each of the three stacks. The set on the right shows only three orientations for each stack; the other three would be generated by the *c* glide operations.

distance is relatively long (3.78 Å). In general, the closest approaches between nonbonded Cl···Cl pairs in different molecules in molecular crystals are about 3.5−3.6 Å.[34,35] 1,4,5,8-Tetrachloronaphthalene crystallizes in a stacked structure with adjacent molecules in the stack rotated by 90°; the separation between molecules along the stacking direction is 3.54 Å.

In the case of the 2,5,8-tri-*tert*-butylphenalenyl radical (**7**),[11] the molecule is slightly distorted from D_{3h} symmetry and has a nearly planar geometry with small deviations of the butyl groups from the plane of the ring. The molecules form discreet face-to-face π-dimers with C···C separations in the range 3.2−3.3 Å (Figure 1). One molecule of the dimer is rotated 60° with respect to the other (as found in the relationship between the superimposed trimers in the 1-dimensional stacks in **1**).

The spacing in the *c* direction of perchlorophenalenyl (**1**), and hence the large intermolecular separation of 3.78 Å within the 1-dimensional stacks, is a direct result of the nonplanarity of the phenalenyl ring system which inhibits the formation of both the 60° rotated stacking motif and the quasisuperimposed structure. Below we discuss the rationale behind the steric constraints imposed by the electronic structure and the propeller geometry of **1** within a one-dimensional stacking motif.



1a **1b**

Figure 5. Stacking requirements of the 60° rotated structure of perchlorophenalenyl (**1**). Because the adjacent peri-chlorine atoms in each pair are displaced in opposite directions, each one of these is forced toward a non-peri-chlorine atom on a neighboring molecule in the stack. This interaction occurs for each of the three sets of peri-chlorine atoms on any given molecule.

The coefficients of the singly occupied nonbonding molecular orbital (NBMO) of the phenalenyl system have approximate 6-fold symmetry (Figure 1, **7a**).[3] Thus, both a completely superimposed structure and a 60° rotated stacking motif (Figure 1, **7b**) lead to almost perfect overlap of the NBMO wave functions in a 1-dimensional stacked geometry and this electronic factor dictates the stacking choices available for both **1** and **7**. While **7** dimerizes in the rotated geometry as a result of the steric bulk of the tertiary butyl groups, due to frustration in the lattice, **1** adopts a 1-dimensional structure that incorporates both stacking motifs. The complexity of the structure of **1** results from the lattice frustration, both intra- and interstack.[33]

Both of the two possible stacking modes of **1** are disfavored by the propeller-type nonplanarity of the molecule (Figure 3). The superimposed structure is disfavored by the eclipsing of the bonds and atoms in successive molecules in the stacks. As may be seen in Figure 4, the molecules rotate slightly (4−5°), to relieve this strict superposition. However, due to the chirality induced by the nonplanarity the molecules (point group D_3) cannot simply rotate in the opposite sense along the stack. Hence the molecules rotate in the same sense, until the interaction with adjacent stacks inhibits a further twist in the stack, and at that point (3 molecules), the 60° rotated structure occurs in the lattice. Thus there are trimers of the quasisuperimposed structure that are related to each other by a 60° rotation. The 60° rotated structure is disfavored by the type of Cl···Cl interactions between adjacent molecules in the stack that are shown in Figure 5. This is again related to the nonplanarity, because in the top molecule of Figure 5, one of the Cl atoms must be displaced toward the lower molecule in the stack as a result of the propeller shape of **1**. The displacement of these chlorine atoms from the mean plane of the molecule amounts to about 0.6 Å, and this can be shown to account for the large intermolecular separation along the stacking axis.[33] Thus the propeller-type nonplanarity of the molecule precludes any type of close approach of neighboring molecules along the stacking axis, and the radicals are well-separated monomers with sterically shielded electron spins.

In the pseudocell structure ($R3m$, $Z = 3$) the three stacks are related by the rhombohedral centering and the molecules within the stacks are related by the *c* translation and the pseudomirror. Even if there were no mirror plane, however, such an arrangement would have impossibly short interstack Cl···Cl interactions (3.26 and 3.27 Å). In the actual structure ($P3c1$, $Z = 18$; see Figure 4) small deviations from the rhombohedral centering and a modulation involving rotations of the molecules around their 3-fold axes relieve these short contacts.

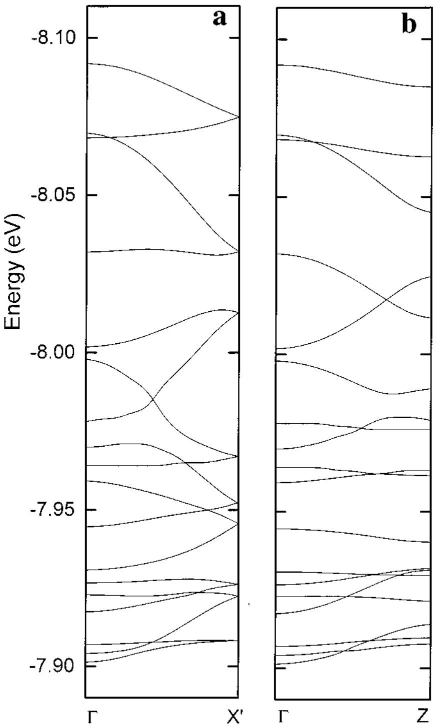


Figure 6. EHT band structure calculated for the experimental (superlattice, $Z = 18$) structure of crystalline **1**. The point X′ is at the boundary of the Brillouin Zone and lies along the intermolecular direction perpendicular to the stacking axis, whereas Z is at (0, 0, $c^*/2$).

Electronic band structure calculations were carried out with Extended Huckel Theory (EHT), using the experimental coordinates from the $P3c1$ unit cell. The energy bands arising from the 18 half-filled NBMOs of perchlorophenalenyl (**1**) are shown in Figure 6. As expected from the structure, the energy bands show little dispersion thus confirming the isolation of the individual molecules as a result of the nonplanar array of chlorine atoms around the phenalenyl nucleus. The first panel in Figure 6 shows the energy bands perpendicular to the stacks and along the directions between molecules, whereas the second panel shows the bands in the stacking direction. The energy dispersions are similar in both directions and have maximum values of about 0.025 eV. The bandwidths (W) for organic semiconductors, metals, and superconductors are about 0.2−0.5 eV, whereas the spiro-biphenalenyl radicals[5] show a maximum bandwidth of about 0.075 eV.

Solid-State Properties of Perchlorophenalenyl (1). The magnetic susceptibility of solid perchlorophenalenyl (**1**) is shown in Figure 7. The solid exhibits Curie paramagnetism over most of the temperature range, until antiferromagnetic ordering sets in below 100 K. A Curie fit to the data in the temperature range 100 to 380 K gives $\theta = 25$ K, and we obtain the number of free spins per molecule (upper panel) using the previous analysis.[5] The weak interaction between molecules (discussed above) accounts for the localized nature of the electron spins. Due to the narrow bandwidth that results from the isolation of the individual molecules, the solid is a Mott−Hubbard insulator, with a room-temperature conductivity of $\rho_{RT} = 10^{-10}$ S/cm.

This behavior contrasts with that seen for the spiro-biphenalenyl radicals,[5] which show nonstacked and well-separated molecules with a Curie magnetic susceptibility, but with a room-temperature conductivity of $\rho_{RT} = 0.05$ S/cm. This difference may be due to the band-filling and its effect on the on-site Coulomb correlation energy. The spiro-biphenalenyl radicals are expected to lead to a $^1/_4$-filled band whereas percholorophenalenyl (**1**) would lead to a $^1/_2$-filled band. Nevertheless, given that it is the propeller-type nonplanarity that leads to the large intermolecular spacing and narrow bandwidth along stacks of **1**, it would be of interest to modify the structure so as to remove the peri-chlorine atoms, perhaps by chalcogenide substitution.[14]

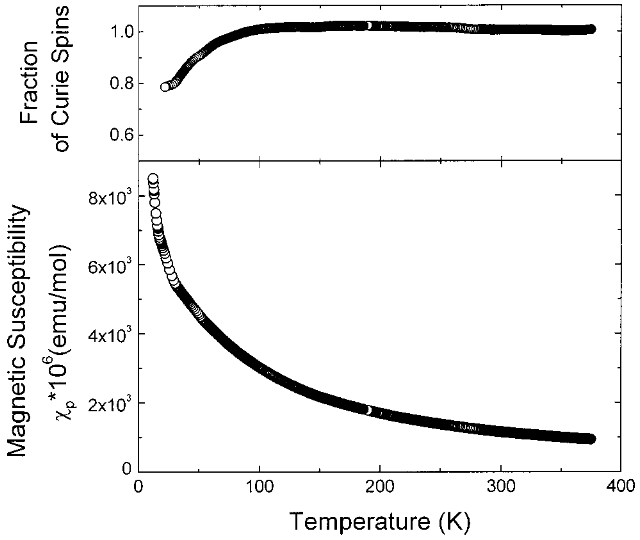


Figure 7. Magnetic susceptibility of crystalline **1** as function of temperature together with the fraction of Curie spins per molecule (see text).

Experimental Section

Solvents (chloroform, 1,2-dichloroethane, and acetonitrile) were distilled from CaH_2 under argon atmosphere prior to use. Glassware was oven dried and set up while hot under an argon atmosphere. Schlenk glassware and techniques were used for the salt and radical forming reactions. Organic extracts were dried with $MgSO_4$ and filtered through fluted filter paper. All reagents and substrates that were not purchased anhydrous were dried under vacuum before use. Ultra dry free flowing gallium trichloride was purchased from Alfa Aesar in sealed ampules and transferred into predried Schlenk glassware in the drybox. Antimony pentachloride (1.0 M solution in CH_2Cl_2) was purchased from Aldrich in sure seal bottles. Reactions and column eluents were monitored by TLC using glass-backed thin-layer chromatography plates (Merck KGaA) viewed under UV light at 254 and 365 nm. Dry flash chromatography on Bodman flash silica 32−63 was used for separations. A Hastelloy B-2 Parr pressure vessel with a glass sleeve and a 600 mL capacity (3000psi limit) was used for the autoclave reactions. Tube sublimations were placed in a Applied Test Systems (ATS) 3210 Tube Furnace and the temperatures were controlled using a Model 3000 Controller. Melting points were determined on a MEL-TEMP capillary melting point apparatus and are uncorrected. Differential scanning calorimetery (DSC) was carried out in hermetically sealed cells on a TA Instruments 2920 modulated DSC apparatus under argon atmosphere. UV−vis spectra were measured on a Shimadzu UV-2501PC spectrophotometer. IR spectra were measured on a Nicole Magma-IR 560 FTIR spectrometer using a Thunderdome ATR accessory with a germanium crystal. ^{13}C NMR spectra were measured on a Varian VXR400 machine, sometimes in the presence of $Cr(acac)_3$ as a relaxation reagent. Microanalyses were carried out by Desert Analytics, Inc.

Perchloroacenaphthylene (10). To a Hastelloy B-2 (Parr Instrument) pressure vessel (600 mL capacity) was added acenaphthene (**8**) (10 g, 64.9 mmol) and phosphorus pentachloride (140 g, 0.67 mol). The reaction vessel was sealed and held at 260 °C for 15 h. On cooling the contents were treated with cold water to destroy unreacted phosphorus pentachloride. The mixture was then extracted (chlorobenzene) and the organic extracts were separated, dried, and filtered. Removal of the volatiles gave a pale orange solid (29 g). Recrystallization of the orange solid gave the title compound **10** (9.3 g, 34%) as orange-red needles, mp 375 °C (from chlorobenzene); $\lambda_{max}(CH_2Cl_2)$/nm 264 (log ϵ 4.83), 301 (3.49), 315 (3.49), 335 sh (3.78), 352 (4.14), 371 (4.33), 384 (3.91); ν_{max}(ATR)/cm^{-1} 1561w, 1496w, 1417w, 1366s, 1305w, 1294w, 1233m, 1160s, 1126s, 889w, 703w; δ_C(100 MHz; CD_2Cl_2) 136.52, 132.97, 132.28, 129.79, 129.23, 124.28, 122.23; *m*/*z* (+EI) clusters at 427.7 (M^+, 100%), 391.7 ($M^+ - Cl$, 20), 355.7 ($M^+ - Cl_2$, 30), 320.7 ($M^+ - Cl_3$, 10), 285.8 ($M^+ - Cl_4$, 18), 250.8 ($M^+ - Cl_5$, 3), doubly charged ions at 213.8 (22), 177.8 (28), 142.9 (10). To the mother liquor was added triphenylphosphine (10.5 g, 40.0 mmol) at ca. 20 °C. The mixture was heated to 150 °C for 0.5 h and on cooling gave by flitration perchloroacenaphthylene (**10**) (14 g, 50%) as orange-red needles, mp 375 °C (from chlorobenzene), identical to an authentic sample. The combined yield for the title compound **10** was 84%. Perchloroacenaphthene (**9**) was isolated pure from a small sample of the crude mixture by chromatography (hexane) as colorless needles, mp >255 °C dec (from hexane); $\lambda_{max}(CH_2Cl_2)$/nm 262 (log ϵ 4.96), 300 (3.74), 314 (3.92), 327 (4.02), 340 (3.91); ν_{max}(ATR)/cm^{-1} 1579w, 1542w, 1430w, 1383m, 1372m, 1298w, 1281m, 1182w, 1150s, 1087s, 997w, 947w, 888w, 850w, 799s, 770w, 732s; δ_C(100 MHz; CD_2Cl_2) 138.06, 134.56, 132.22, 131.44, 129.24, 124.34, 94.54.

Conversion of Perchloroacenaphthene (9) into Perchloroacenaphthylene (10). To a stirred suspension of perchloroacenaphthene (**9**) (700 mg, 1.40 mmol) in chlorobenzene (5 mL) at 20 °C was added triphenylphosphine (385 mg, 1.43 mmol) in one portion. The color of the reaction mixture became dark red and a voluminous orange red precipitate appeared. TLC analysis indicated near total consumption of the triphenylphosphine. The reaction mixture was heated (140 °C) to dissolve the precipitate and on cooling long orange needles were obtained; filtration and washing with a small amount of chlorobenzene then methanol gave perchloroacenaphthylene (**10**) (500 mg, 83%) as orange-red needles, mp 375 °C (from chlorobenzene), identical to that described above.

Perchloro-7*H*-cyclopropano[*a*]acenaphthylene (11). To a vigorously stirred solution of perchloroacenaphthylene (**10**) (5.00 g, 11.68 mmol) and 18-crown-6 (500 mg) in chloroform (600 mL) at 95 °C, under argon was added aqueous KOH (400 g, 200 mL H_2O) in four equal portions over a 20 min period. After a further 10 min the reaction mixture was quenched with water and the organic layer was separated, dried, and filtered. The volatiles were removed to afford a sweet smelling beige colored slurry. The slurry was diluted with acetone and filtered, and the residue was washed twice with cold acetone. Recrystallization of the residue gave the perchloro-7*H*-cyclopropano[*a*]acenaphthylene (**11**) (2.39 g, 40%) as colorless needles, mp >193 °C dec (from cyclohexane); $\lambda_{max}(CH_2Cl_2)$/nm 262 (log ϵ 4.99), 302 (3.72), 316 (3.97), 330 (4.09), 345 (3.97); ν_{max}(ATR)/cm^{-1} 1593w, 1579w, 1542m, 1436w, 1382m, 1371m, 1296m, 1281m, 1215w, 1205w, 1158s, 1131m, 1057w, 1015w, 966s, 883m, 869m, 824w, 785w, 703w; δ_C(100 MHz; CD_2Cl_2) 136.85, 135.41, 133.08, 132.08, 131.58, 123.90, 74.87 (Ar**C**Cl), 61.87 (**C**Cl_2); *m*/*z* (+EI) clusters at 474.7 ($M^+ - Cl$, 100%), 439.7 ($M^+ - Cl_2$, 5), 402.8 ($M^+ - Cl_3$, 35), 367.8 ($M^+ - Cl_4$, 3), 332.8 ($M^+ - Cl_5$, 18), doubly charged ions at 237.3 (10), 201.4 (25), 166.4 (10).

Perchlorophenalenium Hexachloroantimonate (12^+, $SbCl_6^-$ and 13^+, $SbCl_6^-$). To a stirred suspension of perchloro-7*H*-cyclopropano-[*a*]acenaphthylene (**11**) (1.07 g, 2.09 mmol) in 1,2-dichloroethane (30 mL) at 85 °C (bath temperature), under argon, (1.0M, CH_2Cl_2) was added antimony pentachloride (8 mL, 8 mmol) dropwise. After 20 min no starting material remained (TLC) and a green microcrystalline precipitate with a golden sheen was observed. The reaction mixture was then allowed to cool to ca. 40 °C, and the precipitate was filtered under argon and washed (1,2-dichloroethane, 2 × 10 mL) to give a mixture of salts (**12**$^+$, $SbCl_6^-$) and (**13**$^+$, $SbCl_6^-$) (1.37 g, 81%) as deep green crystals which when ground gave a fine red powder, mp >300 °C dec (Found: C, 19.27; Cl, 65.58; Sb, 15.05. $C_{13}Cl_{15}Sb$ requires C, 19.27; Cl, 65.69; Sb, 15.04); ν_{max}(ATR)/cm^{-1} 1499s, 1462m, 1354w, 1329w, 1306m, 1268m, 1199w, 1159s, 1099w, 1000m, 841w, 710w.

Isolation of (2,2,3,4,5,6,7,8-Octachloro-1*H*,2*H*-acenaphthyl-1-ylidene)-dichloromethane (14), 2,2,3,4,5,6,7,8-Octachloro-1*H*,2*H*-acenaphthylen-1-one (15), (1-Oxo-1*H*,2*H*-3,4,5,6,7,8-hexachloroacenaphthyl-2-ylidene)-dichloromethane (16), and 2,3,4,5,6,7,8,9-Octachloro-1*H*-phenalen-1-one (17). The dark red filtrate from the above procedure was treated with water to give a bright yellow solution containing a white precipitate. The mixture was extracted (CH_2Cl_2) and the organic extracts were dried and filtered. Adsorption onto silica followed by dry flash chromatography (hexane/CH_2Cl_2) gave (2,2,3,4,5,6,7,8-octachloro-1*H*,2*H*-acenaphthyl-1-ylidene)-dichloromethane (**14**) as colorless needles, mp 175−178 °C (from cyclohexane) (Found: C, 30.42; Cl, 69.50. $C_{13}Cl_{10}$ requires C, 30.56; Cl, 69.44%); $\lambda_{max}(CH_2Cl_2)$/nm 235 (log ϵ 4.46), 263 sh (4.69), 270 (4.76), 286 sh (4.26), 335 sh (4.03), 352 (4.18), 373 sh (4.09); ν_{max}(ATR)/cm^{-1} 1586m, 1573m, 1537w, 1421w, 1383m, 1372m, 1293m, 1280m, 1269m, 1177w, 1156s, 1096s, 1059s, 988s, 974w, 918m, 876w, 821w, 804s, 777m, 740m, 703w, 695w; δ_C(100 MHz; CD_2Cl_2) 138.52, 138.39, 137.54, 136.73, 133.41, 131.40, 130.82, 130.80, 130.24, 130.19, 128.29, 123.82, 83.58 (**C**Cl_2); *m*/*z* (+EI) clusters at 509.8 (M^+, 6%), 474.8 ($M^+ - Cl$, 100), 439.7 ($M^+ - Cl_2$, 2), 427.8 ($M^+ - CCl_2$, 8), 402.8 ($M^+ - Cl_3$, 24), 367.9 ($M^+ - Cl_4$, 4), 332.9 ($M^+ - Cl_5$, 16), 297.9 ($M^+ - Cl_6$, 3), 260.9 ($M^+ - Cl_7$, 6), doubly charged ions at 237.4 (16), 201.4 (22), 166.4 (11). Further elution gave 2,2,3,4,5,6,7,8-octachloro-1*H*,2*H*-acenaphthylen-1-one (**15**) as colorless prisms, mp 226−228 °C (from cyclohexane) (Found: C, 32.63; Cl, 63.97. $C_{12}Cl_8O$ requires C, 32.46; Cl, 63.93%); $\lambda_{max}(CH_2Cl_2)$/nm 256 (log ϵ 4.90), 284 (4.21), 335 sh (3.75), 350 (3.87), 379 sh (3.75); ν_{max}(ATR)/cm^{-1} 1755s (C═O), 1580w, 1543m, 1425w, 1377m, 1366m, 1299w, 1276m, 1182m, 1164m, 1084s, 1042w, 992w, 953w, 875w, 837m, 789w, 770w, 739w, 700m; δ_C(100 MHz; CD_2Cl_2) 185.46 (**C**═O), 138.51, 138.00, 137.87, 136.84, 134.43, 132.23, 132.20, 132.04, 124.58, 123.01, 77.23 (**C**Cl_2); *m*/*z* (+EI) clusters at 443.8 (M^+, 22%), 406.8 ($M^+ - Cl$, 100), 378.8 ($M^+ - COCl$, 18), 372.9 ($M^+ - Cl_2$, 13), 344.9 ($M^+ - COCl_2$, 6), 308.9 ($M^+ - COCl_3$, 24), 274.9 ($M^+ - COCl_4$, 4), 238.9 ($M^+ - COCl_5$, 8), doubly charged ions at 221.4 (3), 203.4 (6), 189.4 (14), 154.4 (13). Further elution gave (1-oxo-1*H*,2*H*-3,4,5,6,7,8-hexachloroacenaphthyl-2-ylidene)-dichloromethane (**16**) as colorless needles, mp 209−210 °C (from cyclohexane) (Found: C, 34.27; Cl, 62.00. $C_{13}Cl_8O$ requires C, 34.24; Cl, 62.25%); $\lambda_{max}(CH_2Cl_2)$/nm 232 (log ϵ 4.40), 266 (5.00), 298 (4.18), 309 sh (4.16), 340 (4.01), 369 sh (3.75); ν_{max}(ATR)/cm^{-1} 1723s (C═O), 1558s, 1525w, 1408w, 1377w, 1363m, 1293m, 1281w, 1264w, 1168s, 1144m, 1106s, 1042s, 995m, 979m, 908m, 839w, 806w, 789w, 766w, 748m, 736w, 695w; δ_C(100 MHz; CD_2Cl_2) 181.37 (**C**═O), 137.86, 137.51, 136.73, 135.63, 135.06, 131.91, 131.36, 130.72, 130.10, 128.69, 126.85, 124.11; *m*/*z* (+EI) clusters at 455.8 (M^+, 100%), 418.8 ($M^+ - CO$, 24), 392.8 ($M^+ - COCl$, 6), 355.9 ($M^+ - COCl_2$, 38), 320.9 ($M^+ - COCl_3$, 6), 285.9 ($M^+ - COCl_4$, 19), 249.8 ($M^+ - COCl_5$, 4), doubly charged ions at 227.9 (5), 213.9 (18), 177.9 (35), 160.4 (6). Further elution gave 2,3,4,5,6,7,8,9-octachloro-1*H*-phenalen-1-one (**17**) as a yellow solid mp 195−198 °C (from cyclohexane); $\lambda_{max}(CH_2Cl_2)$/nm 229 (log ϵ 4.57), 293 (4.66), 376 (4.00), 403 (4.06), 443 (3.85); ν_{max}(ATR)/cm^{-1} 1667s (C═O), 1571m, 1498s, 1410m, 1357w, 1338m, 1293s, 1219w, 1190m, 1152s, 1056s, 988s, 903w, 872w, 804w, 796w, 768w, 744w, 719w; δ_C(100 MHz; CD_2Cl_2) 174.48 (**C**═O), 139.68, 139.65, 138.52, 138.30, 137.26, 136.91, 136.63, 134.30, 127.23, 126.04, 124.14, 123.97; *m*/*z* (+EI) clusters at 455.7 (M^+, 80%), 427.7 ($M^+ - CO$, 100), 392.7 ($M^+ - COCl$, 5), 357.8 ($M^+ - COCl_2$, 50), 320.8 ($M^+ - COCl_3$, 5), 285.8 ($M^+ - COCl_4$, 35), doubly charged ions at 213.9 (45), 177.9 (60), 160.4 (15).

Perchlorophenalenium Tetrachlorogallate (12^+, $GaCl_4^-$). To a stirred suspension of perchloro-7*H*-cycloprop[*a*]acenaphthylene (**11**) (1.00 g, 1.96 mmol) in 1,2-dichloroethane (40 mL) at 20 °C, under argon (1.0 M, 1,2-dichloroethane), was added gallium trichloride (4 mL, 4 mmol) in one portion. A red coloration was observed but after 3 h the starting material remained in suspension and no precipitation was observed. The reaction mixture was warmed to 90 °C for 30 min to give a clear deep red-violet colored solution. The reaction mixture was then allowed to cool to 20 °C, and on removal of a 1 mL portion by syringe for analysis bright green crystals precipitated from the reaction mixture. The precipitate was filtered under argon and washed with cold 1,2-dichloroethane to give perchlorophenalenium tetrachlorogallate (**12**$^+$, $GaCl_4^-$) (1.17 g, 87%) as a dark green microcrystalline salt which when ground gave a fine red powder, mp >300 °C dec (Found: C, 22.90; Cl, 67.39; Ga, 9.73. $C_{13}Cl_9Ga$ requires C, 22.72; Cl, 67.13; Ga, 10.15%); ν_{max}(ATR)/cm^{-1} 1535w, 1508m, 1455m, 1351w, 1312m, 1266m, 1161s, 1132m, 1001m, 789w, 773w; *m*/*z* (+EI) clusters at 474.8 ($M^+ - GaCl_4$, 100%), 439.8 ($M^+ - GaCl_5$, 10), 402.9 ($M^+ - GaCl_6$, 40), 367.9 ($M^+ - GaCl_7$, 7), 332.9 ($M^+ - GaCl_8$, 23), 297.9 ($M^+ - GaCl_9$, 5), 262.9 ($M^+ - GaCl_{10}$, 8), 177.9 ($GaCl_3$, 25), 140.9 ($GaCl_2$, 65), doubly charged ions at 237.4 (15), 201.4 (30), 166.4 (10). The dark red filtrate was treated with water to give a bright yellow solution. The solution was extracted (CH_2Cl_2) and the organic extracts were dried and filtered. TLC analysis of the filtrate identified perchlorophenalenone (**17**) together with several other unidentified minor compounds.

Perchlorophenalenyl (1). To an intimate mixture of perchlorophenalenium tetrachlorogallate (**12**$^+$, $GaCl_4^-$) (511 mg, 0.74 mmol) and anhydrous *n*-tetrabutylammonium iodide (275 mg, 0.75 mmol), at ca. 20 °C, under argon, was added acetonitrile (5 mL) in one portion. The reaction mixture was rapidly stirred and the green salt quickly converted into a yellow precipitate which became olive-green within several minutes. After 20 min the olive-green precipitate was filtered under argon and washed twice with acetonitrile to give perchlorophenalenyl (**1**) (crude 341 mg, 96%) as an olive-green powder, mp >160 °C dec The crude product gave a strong EPR signal and appeared to consist of a single compound by TLC (hexane), ν_{max}(ATR)/cm^{-1} 1667w, 1567w, 1503w, 1454s, 1351w, 1291w, 1281w, 1230w, 1151s, 1056w, 988s, 825m, 763w. 741w. Repeated sublimation (3-zone furnace, 5×10^{-5} Torr, 105−150 °C) of the crude product gave **1** (550 mg, 41% from crude) as black hexagonal crystals, mp >180 °C dec (DSC mp 248 °C) (Found: C, 32.95; Cl, 67.06. $C_{13}Cl_9$ requires C, 32.84; Cl, 67.16); ν_{max}(ATR)/cm^{-1} 1453s, 1420w, 1351w, 1329w, 1290w, 1281w, 1268w, 1234w, 1150s, 1057w, 988s, 825w; *m*/*z* (+EI) clusters at 474.8 (M^+, 100%), 439.8 ($M^+ - Cl$, 3), 402.8 ($M^+ - Cl_2$, 30), 367.9 ($M^+ - Cl_3$, 3), 332.9 ($M^+ - Cl_4$, 19), 297.9 ($M^+ - Cl_5$, 2), 262.9 ($M^+ - Cl_6$, 5), doubly charged ions at 237.4 (11), 201.4 (22), 166.4 (12).

Cyclic Voltammetry. Cyclic voltammetry was performed on a computer controlled Pine AFCBP1 bipotentiostat, using scan rates of 50−100 mV s^{-1} on solutions of **1** containing 0.1 M tetra-*n*-butylammonium hexafluorophosphate in CH_2Cl_2 or CH_3CN (both dried by distillation from P_2O_5). Potentials were scanned from −0.5 to 1.5 V with respect to the quasireference electrode in a single compartment cell fitted with Pt electrodes and referenced to the ferrocenium/ferrocene couple at 0.48 (CH_2Cl_2) and 0.38 V (CH_3CN) vs SCE.[28]

Crystal Structure Determination. Crystals of perchlorophenalenyl ($C_{13}Cl_9$, **1**) are hexagonal prisms elongated along *c*; $a = b = 18.704(3)$ Å, $c = 22.675(4)$ Å, $V = 6870(2)$ Å^3 at 299 K. Data (1475 1° frames) were measured on Nonius CCD diffractometer using graphite-monochromated Mo Kσ radiation. The structure was solved with the program SIR92[36] in the trigonal space group *P*3*c*1 with 9 independent molecules in the unit cell, each of which is located on a 3-fold rotation axis. The structure is a modulated superstructure that presents a number of refinement difficulties, but refinement in a pseudocell having $c = 22.675$ Å/6 = 3.7792 Å was straightforward. The symmetry operations of the pseudocell are those of space group *R*3*m*. The molecules appear to be disordered across the mirror planes, which are the projections of the *c* glide planes of group *P*3*c*1. Final agreement factors for 64 variables are $R = 0.040$ (on *F*; the 318 reflections having $I > 2\sigma_I$) and $wR = 0.100$ (on F^2; all 323 reflections). The distances and angles, which are determined for atomic positions averaged over nine independent molecules, are reasonably precise but rather inaccurate. The atomic ellipsoids also show the effects of the averaging, but are physically reasonable. Details of the superstructure refinement will appear shortly.[33]

Magnetic Susceptibility Measurements. The magnetic susceptibility was measured over the temperature range 5−400 K on a George Associates Faraday balance operating at 0.5 T.

Conductivity Measurements. As a result of the high resistivity of the sample, the single-crystal conductivity (σ) of **1** was measured in a two probe configuration, and the experiment therefore provides an upper limit on the intrinsic conductivity. Measurements along and perpendicular to the crystal axis showed that the conductivity was approximately isotropic.

Band Structure Calculations. The band structure calculations made use of a modified version of the extended Huckel theory (EHT) band structure program supplied by M.-H. Whangbo. The parameter set is chosen to provide a reasonably consistent picture of bonding in heterocyclic organic compounds.[37,38]

Acknowledgment. This work was supported by the Office of Basic Energy Sciences, Department of Energy under Grant No. DE-FG02-97ER45668.

Supporting Information Available: A crystallographic information file (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

JA0018015

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