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1,9-DISUBSTITUTED PHENALENES—I

SYNTHESIS OF N- AND S-DERIVATIVES OF 9-HYDROXY-1-PHENALENONE

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Abstract—The reaction of 9-hydroxy-1-phenalenone with Ag_2O and alkyliodides gives the analogous β-keto-ethers from which synthetic pathways have been devised to isolate and characterise some nitrogen and sulphur derivatives. As intermediates stable phenalenium cations can be isolated by the reaction of 9-substituted 1-phenalenones with $[(C_2H_5)_3O]^+BF_4^-$. Whenever possible, a strong intramolecular H-bond is formed between the 1- and 9-substituents as shown by the low-field resonances of the respective hydrogens in the ^1H NMR and the stability of the compounds towards reduction.

In connection with our research project on electron rich planar d^8 complexes,[1] the 1,9-ditheterophenalenes are of interest as potential chelating ligands. 9-Hydroxy-1-phenalenone,[2] (1), can be regarded as a β-hydroxy-ketone and this has the same chelating group as the enol form of 2,5-pentanedione (acac) and related compounds. Complexes of 1 have recently been synthesised [3] but attempts to prepare ligands and complexes of the potentially more back-bonding N- and S-derivatives of 1 by methods analogous to those for other α- and β-hydroxy-ketones[4] have so far failed.[1,2b,5]

The reason lies in the incorporation of the chelate group into the well developed π-system of the polycycle. The very strong intramolecular H-bond prevents a nucleophilic substitution on 1- or 9-position.[6] Nevertheless, it is possible to devise a synthetic pathway leading to the replacement of oxygen by the more polarisable N and S atoms.

RESULTS

We have found that the 9-alkoxy-1-phenalenones(**2a–d**), can be formed in high yields by a modified Ag_2O/Alkyl-I method.[7] They provide convenient starting materials for further synthesis (Fig. 1).

The β-keto-ethers quite readily undergo a nucleophilic substitution by secondary or primary amines but do not react with ammonia. Primary alkylamines give 9-alkylamino-1-phenalenones, (**3a, d**), the H-bond between N and O preventing a further condensation with the oxygen. With ethanolic dimethylamine compounds (**2a–d**) form 9-dimethylamino-1-phenalenone, (4), which can be converted with H_2S into 9-thiolo-1-phenalenone, (5). Again, the exchange of the second oxygen can not be achieved by nucleophilic substitution. This is prevented either by the strong H-bond—as in cases of 3 and 5—or by the single bonded substituent —as in 4 for instance—being removed by aminolysis or thiolysis.

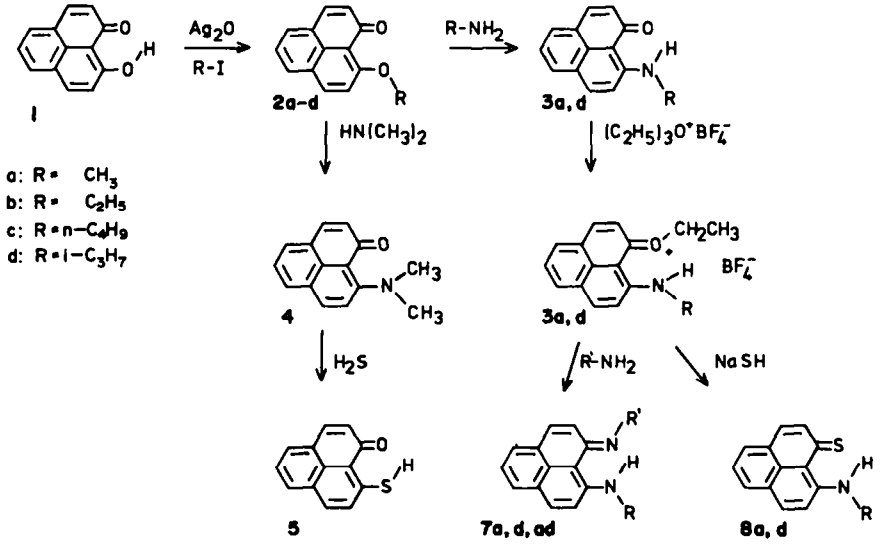

Fig. 1. Reaction scheme for substitution at the 1- and 9-positions of 9-hydroxy-1-phenalenone.

McGeachin has shown that β-amino-ketones are activated by treatment with $[(C_2H_5)_3O]^+BF_4^-$ (Meerwein's salt).[8] Likewise **3a** and **3d**, after treatment with Meerwein's salt, can be alkylated to 9-alkylamino-1-ethoxyphenalenium tetrafluoroborates, (**6a, d**). The OEt group of the phenalenium salts is easily removed by amines and sulfides (**7a, d, 8a, d**).

For our purpose, we were interested in totally planar ligands and therefore had to find a modification of the synthetic pathway because the β-keto-ethers, (**2a–d**), would not react with NH_3 under various conditions. Accordingly the direct alkylation of these compounds was investigated. Depending on the size and steric requirements of the ether substituents, two structural isomers are formed. The reaction of the ethoxy derivative, (**2b**), with Meerwein's salt yields only as a by-product (30%) 1,9-bisethoxyphenalenium tetrafluorobate, (**9**), in which both substituents are exchanged with methylamine to give **7a** (Fig. 2). The major product (60%) is 9-diethyloxonium-1-phenalenone tetrafluoroborate, (**10**), which reacts only with one equivalent methylamine to form **3a**.

1-Ethoxy-9-n-butoxyphenalenium tetrafluoroborate, (**11**), is the only isomer (Fig. 3) produced by the alkylation of **2d**. This reacts with NH_3—through the intermediates (**12** and **13**)—to yield 9-amino-1-phenalenimine, (**14**), the first known stable β-iminoamine.[9]

EXPERIMENTAL

9-Hydroxy-1-phenalenone, (**1**), was prepared by the method of Koelsch and Anthes[2] but using 1,2-dichloroethane as solvent for the cyclisation. The ^1H NMR spectra were measured on a Jeol-Minimar 100 MHz instrument. The electrochemical values have been obtained on a three electrode Princeton Applied Research Model 170 instrument with Pt working and auxiliary electrode *vs* Ag/AgCl reference electrode. The uncorrected melting points were determined on a Reichert microscope heating block. The analytical results for carbon in the tetrafluoroborate salts have a systematic error of approximately 1% absolute.

9-*Alkoxy*-1-*phenalenones*, (2a–d)

General method. Compound **1** (29.4 g; 150 mM) Ag_2O (34.8 g; 150 mM) (Johnson Matthey Chemicals Ltd.) and 50 mM R–I were refluxed under intense stirring in 500 ml $CHCl_3$. After 2, 4 and 6 hr, additional 50 mM of alkyliodide were added and the yellow soln filtered from the gray-brown residue after 7 hr. The residue was washed several times with chloroform and the combined filtrate was evaporated until excess alkyl-iodide was removed and a dark-yellow brown oil remained which could be used without further purification. This solidified overnight to a yellow cake and could be recrystallized from *n*-heptane/benzene, or purified by column chromatography on Al_2O_3 (0.05–0.2 mm) with $CHCl_3$ (yields vary between 80 and 90%).

Compound **2a** m.p. 81°. (Calc.: C, 79.99; H, 4.79. Found: C, 79.48; H, 4.68%).

Compound **2b** m.p. 74°. (Calc.: C, 80.34; H, 5.39. Found: C, 79.70; H, 5.70%).

Compound **2c** m.p. 65°. (Calc.: C, 80.93; H, 6.39. Found: C, 80.80; H, 6.43%).

Compound **2d** characterised by the parent ion in the mass spectrum, ^1H NMR (δ, TMS_i: 1.52 (CH_3), 4.9 (CH), 6.6 (H_8), 7.4 (H_2), 7.62 (H_7), 8.08 (H_3)).

9-*Methylamino*-1-*phenalenone*, (3a)

30% Ethanolic methylamine solution (20 ml) was dropped into 5 mM of the ether (**2a, 2b, 2c,** or **2d**) in 50 ml CH_2Cl_2. After removal of the solvent, **3a** could be recrystallised from n-heptane/chloroform in nearly quantitative yield, **3a** m.p. 112°. (Calc.: C, 80.36; H, 5.30; N, 6.69. Found: C, 80.70; H, 5.29; N, 6.47%).

9-*Dimethylamino*-1-*phenalenone*, (4)

The reaction proceeded similarly to **3a** using a 30% ethanolic solution of dimethylamine and recrystallising the intense red

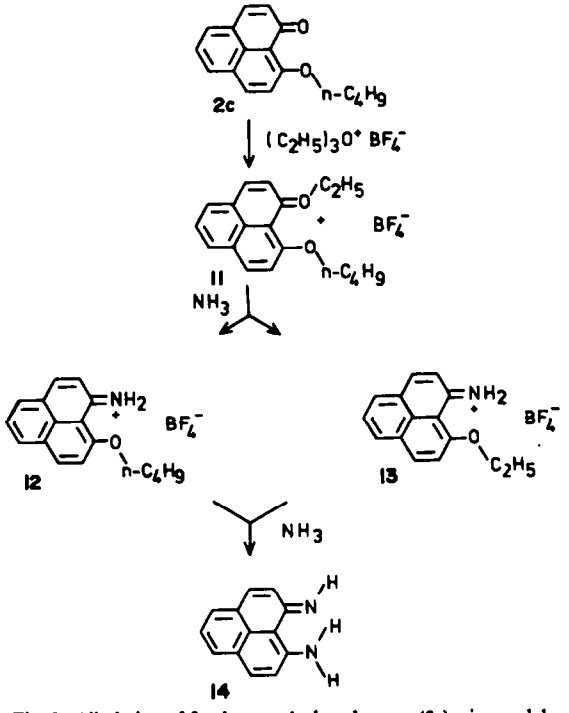

Fig. 3. Alkylation of 9-n-butoxy-1-phenalenone, (**2c**), gives solely the bis-alkoxy product, (**11**), which reacts with NH_3 to the stable 9-amino-1-phenalenimine, (**14**).

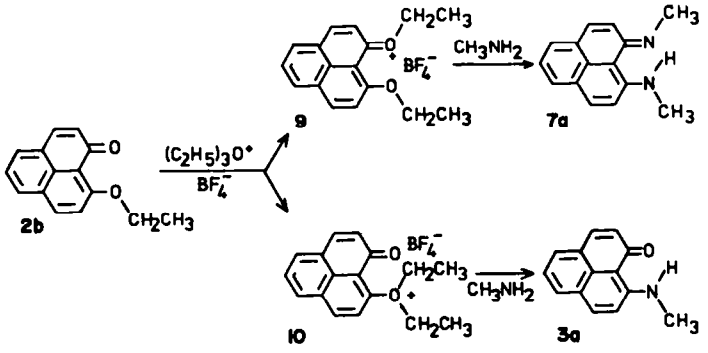

Fig. 2. Alkylation of 9-ethoxy-1-phenalenone, (**2b**), gives two isomers, (**9**) and (**10**), which react differently with methylamine.

compound from n-heptane, 4 m.p. 82°. (Calc.: C, 80.69; H, 5.87; N, 6.27. Found: C, 81.06; H, 5.87; N, 6.22%).

9-Thiolo-1-phenalenone, (5)

Compound 4 (4.2 g; 20 mM) was dissolved in 100 ml MeOH and H_2S was bubbled slowly through the soln for 2 hr. 3.2 g (75%) dark red crystals of 5 precipitated and were recrystallized from $CHCl_3$, m.p. 171°. (Calc.: C, 73.56; H, 3.80; S, 15.04. Found: C, 73.83; H, 4.11; S, 14.99%).

9-Isopropylamino-1-ethoxyphenalenium tetrafluoroborate, (6d)

$[(C_2H_5)_3O]^+BF_4^-$ (4.6 g; 22 mM) in 30 ml CH_2Cl_2 was added to a soln of 3d (4.8 g; 20 mM)—obtained analogous to 3a—in 50 ml CH_2Cl_2. 6 g (85%) of 6d precipitated and were recrystallised from $CHCl_3/CH_3CN$, decomp. 160°. (Calc.: C, 61.39; H, 5.44; N, 3.98; B, 3.07; F, 21.58. Found: C, 60.27; H, 5.43; N, 3.61; B, 3.0; F, 21.3%).

9-Alkylamino-1-alkyliminophenalene, (7a, 7d, 7ad)

The corresponding tetrafluoroborate salt, (6a or 6d), was treated in CH_2Cl_2 with two equivs of the alkylamine yielding almost quantitatively 7a, 7d, or the unsymmetrically substituted 7ad, which were recrystallised from n-heptane.

Compound 7a m.p. 147°. (Calc.: C, 81.05; H, 6.35; N, 12.60. Found: C, 80.78; H, 6.47; N, 12.66%).

Compound 7d m.p. 197°. (Calc.: C, 81.97; H, 7.98; N, 10.06. Found: C, 81.89; H, 7.70; N, 10.30%).

Compound 7ad m.p. 109°. (Calc.: C, 81.56; H, 7.25; N, 11.19. Found: C, 81.06; H, 7.26; N, 11.05%).

9-Alkylimino-1-phenalenethione, (8a, 8d)

A soln of 15 mM (6a or 6d) in 70 ml MeOH was stirred for 4 hr with 1.7 g NaSH at room temp. The brown residue was recrystallised from $CHCl_3$ to give, in 75–85% yield, (8a or 8d).

Compound 8a m.p. 127°. (Calc.: C, 74.63; H, 4.92; N, 6.22; S, 14.23. Found: C, 75.00; H, 4.96; N, 6.11; S, 13.91%).

Compound 8d m.p. 129°. (Calc.: C, 75.85; H, 5.97; N, 5.53; S, 12.65. Found: C, 76.17; H, 6.09; N, 5.47; S, 12.53%).

1,9-Diethoxyphenalenium tetrafluoroborate, (9), *and 9-diethyloxonium-1-phenalenone*, (10)

$[(C_2H_5)_3O]^+BF_4^-$ (11 g; 50 mM) was dissolved in 50 ml CH_2Cl_2 and added to a stirred soln of 2b (11 g; 50 mM) in 30 ml CH_2Cl_2. After 3 hr the yellow ppt (14.5 g, 83%) was collected and crystallised fractionally from MeCN giving 9.5 g (10) and 3.2 g (9)—the more soluble isomer. (9) m.p. 209°, (10) decomp. 110°. (Calc.: C, 60.03; H, 5.04; B, 3.18; F, 22.34. Found: C, 59.03; H, 4.96; B, 3.1; F, 22.6%). The reaction of 9 with excess ethanolic $MeNH_2$ gives quantitatively 7a, while 10 forms 3a.

9-n-Butoxy-1-ethoxyphenalenium tetrafluoroborate, (11)

$[(CH_3CH_2)_3O]^+BF_4^-$ (11 g; 50 mM) was dissolved in 50 ml CH_2Cl_2 and added to a stirred soln of 2c (12.6 g; 50 mM) in 30 ml CH_2Cl_2. After 3 hr, 50 ml n-heptane was added and the yellow ppt separated and recrystallised from CH_2Cl_2 (15.6 g, 85%), yielding 11 m.p. 148°. (Calc.: C, 61.98; H, 5.75; B, 2.94; F, 20.64. Found: C, 61.66; H, 5.70; B, 2.8; F, 20.3%).

9-Amino-1-phenalenimine (14)

Compound 11 (7.4 g; 20 mM) was suspended in 150 ml $CHCl_3$ and dry NH_3 was bubbled through the mixture. After at least 4 hr, 50 ml n-heptane was added to the soln and NH_4BF_4 precipitated. The soln was evaporated and the residue recrystallised from n-heptane (2.9 g, 74%), yielding 14, m.p. 88°. (Calc.: C, 80.39; H, 5.20; N, 14.42. Found: C, 80.23; H, 5.22; N, 14.00%).

When the passage of NH_3 was stopped after 1 hr, some intermediates could be separated from the concentrated $CHCl_3$/n-heptane mixture. The alkoxy-imonium salts, (12 and 13), could be determined by their characteristic alkyl resonances in the ^1H NMR spectra and 12 could be isolated for analysis, m.p. 232°. (Calc.: C, 57.91; H, 4.54; N, 4.50; B, 3.47; F, 24.43. Found: C, 56.76; H, 4.75; N, 4.13; B, 3.6; F, 24.3%).

DISCUSSION

The key reaction in the chemistry of 1,9-disubstituted phenalenes is the breaking of the strong H-bond of 1 to form β-keto-ethers, (2a–d). The consequential rearrangement of electron distribution is apparent from the marked shifts in the ^1H resonances of 2a compared with those of 1 (Table 1).[10] The increase in the first reduction potential from −0.95 V (1) to −1.11 V (2a) is consistent with the assumption of a loss in resonance energy enlarging the HOMO–LUMO separation. This shift is greater

Table 1. ^1H NMR[a] data and reversible half-wave reduction potentials[b] of 1,9-phenalenes

No.	X	Y	H_y	H_2	H_3	H_7	H_8	$E_{\frac{1}{2}}$
(1)[c]	O	HO	14.8	7.02	7.98	7.98	7.02[d]	−0.95[e]
(2a)	O	OCH_3		7.35	8.0	7.56	6.68[d]	−1.11[e]
(3a)	O	$HNCH_3$	11.86	6.93	7.7	7.76	6.97[d]	−1.27[e]
(4)	O	$N(CH_3)_2$		multiplet		7.2 − 8.1[d]		−1.03[e]
(5)	O	HS	16.6	multiplet		7.2 − 8.1[d]		−0.63[e]
(6a)$^+$	OCH_2CH_3	$HNCH_3$	9.9	multiplet		7.0 − 8.2[f]		−0.39[g]
(7a)	NCH_3	$HNCH_3$	13.5	7.15	7.63	7.63	7.15[d]	irrev.[e]
(8a)	S	$HNCH_3$	15.6	multiplet		7.2 − 7.9[d]		−0.97[e]
(9)$^+$	OCH_2CH_3	OCH_2CH_3		7.6	8.67	8.67	7.6[f]	−0.07[g]
(10)$^+$	O	$O(CH_2CH_3)_2$		6.9	8.12	8.46	7.58[f]	irrev.[g]
(12)$^+$	OCH_2CH_3	HNH	9.0	multiplet		6.8 − 8.4[f]		−0.39[g]
(14)	HN	HNH	8.22	6.59	7.42	7.42	6.59[d]	irrev.[e]

[a] Shifts in δ *vs.* TMS_i; X- and Y-substituents and $H_{4,5,6}$-occurring between H_{2-8} are not listed. [b] $E_{\frac{1}{2}}$ *vs.* Ag/AgCl reference electrode. [c] Reference 1.

[d] $CDCl_3$ solution. [e] In acetone saturated with $(CH_3CH_2)_4NClO_4$. [f] CD_3CN solution.

[g] In CH_3CN saturated with $(CH_3CH_2)_4NClO_4$.

than one would expect for a simple substituent effect.[11] It points into the same direction as the difference of the first π-π^* transition [1 22,700 cm^{-1}, $\epsilon = 9600\,cm^{-1}\,mol^{-1}$: **2a** 22,400 cm^{-1}, 10,900 $cm^{-1}\,mol^{-1}$].

As unsaturated β-keto-ethers, the reactions of **2a–d** with primary amines to yield **3a–d** are like those of the parent compound 3-ethoxy-propenone.[12] The planar geometry favours the formation of a H-bond, yet not quite so strong as in the other cases. This can be seen from the ^1H NMR of the relevant proton in **3a** but also from its coupling of 6 Hz to the Me-group which agrees with similar values for other β-amino-ketones discussed by Dudek *et al.*[13]

The closer bond of the hydrogen in **3a, d** to the nitrogen, thus lowering its basicity, is one of the contributing factors for the alkylation of the oxygen by Meerwein's salt. In general, when the alkylation takes place on the 1-oxygen, the products can be regarded as 1,9-substituted phenalenium salts (Fig. 4). The distribution of the positive charge over the π-system of the ring[14] and the stability of the resulting cations is also common to other phenalene species.[15]

Compounds **6a** and **6d** react readily with amines and sodium hydrogen sulfide to give **7** and **8** as is also shown for their analogous acac derivatives.[16] It is now possible to compare the effect of the 1-substituents O, N and S with different electronegativities in the series **3a**, **7a**, **8a**. In terms of a simple MO model, the HOMO–LUMO separation decreases with the less electronegative substituent[10] as shown in Fig. 5 by the electronic absorption spectra. This bathochromic shift should also be due to the lowering of the LUMO energy as is consistent with the trend of the reversible reduction potentials.

The formation of 9-thiolo-1-phenalenone corresponds to the method of Mayer by treating a β-dialkylamino-ketone with H_2S.[17] As for the compounds **1**, **3**, **7** and **8**, the resonance above 10 ppm in the ^1H NMR indicates the bridging position of the proton between the 1,9-substituents. The shift is nearly identical to other β-thiolo-ketones in nonpolar solvents at low temperature where these compounds exist only in their enol forms.[18] The stability of the radical anions, especially of compounds with the H-bond in the neutral state, shows again the dominating role of the ring system (Fig. 4).

Like the alkylation products of the amino-ketones, the keto-ethers are also converted into very stable phenalenium salts. The attack of Meerwein's salt can occur on both O atoms (Fig. 2) but the distribution of the isomers is influenced by the nature of the alkyl chain. The two isomers of the ethyl derivative can be separated by fractional crystallisation from MeCN and distinguished and assigned by differences in their reactivity, redox behaviour, IR, ^1H and ^{13}C NMR spectra, and their reactions with $MeNH_2$. The ready attack on the ether group is surprising because normally aryl-ethers do not react with tertiary oxonium salts.[19] The symmetrically

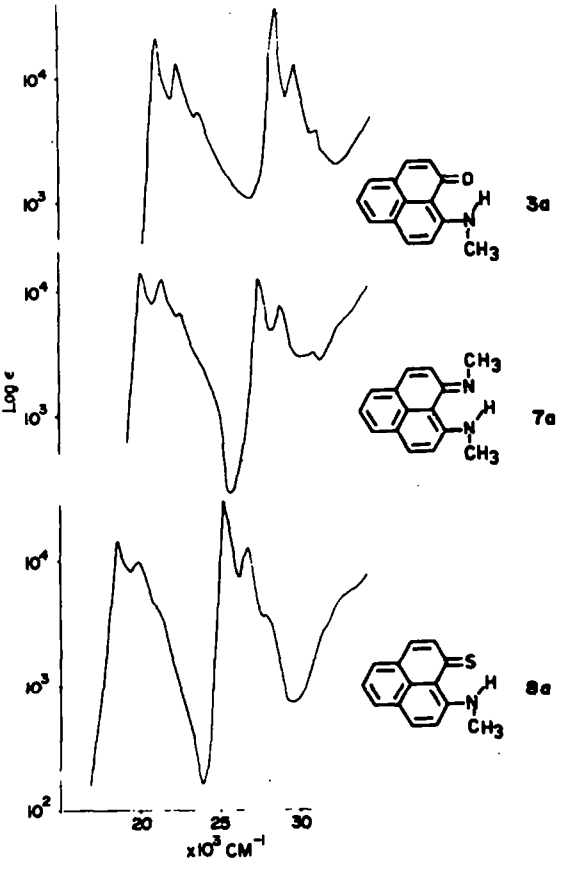

Fig. 5. Bathochromic shift of the electronic absorption under the influence of the 1-substituent (c-C_6H_{12} as solvent).

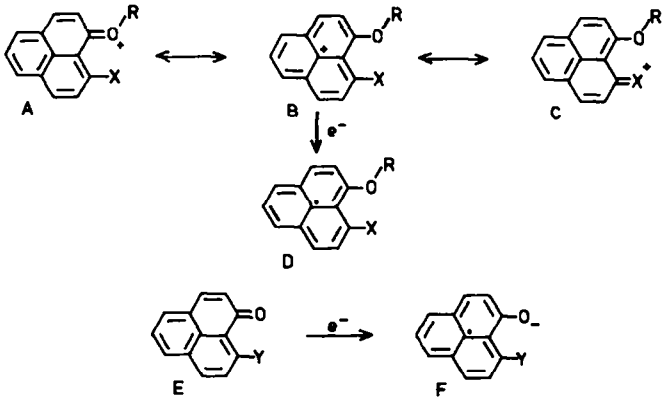

Fig. 4. Delocalisation of the positive charge over the π-system with the mesomers A, B and C, and the reduction to a phenalenyl derivative, D. The stability of the reduction products F from E is also due to the conjugation into the ring.

alkylated and resonance stabilised phenalenium salt is favoured (Fig. 4) by increasing the chain size.

The cations of **6**, **9** and **12**, undergo a reversible reduction at low potentials (Table 1) forming 1,9-disubstituted derivatives of the known radical phenalenyl.[20] There is no indication of any H-bond in the aminophenalenium salts (**6a,d** and **12**). The N–H stretching frequencies appear between 3200 and 3300 cm^{-1} and the protons occur in the ^1H NMR spectra below $\delta = 10$ ppm.

Both alkoxy groups of **9** and **11** are successively exchanged with amines yielding the aminoimines (**7a,d** and **14**). The unsubstituted compound **14** is of special interest: all three protons on the two nitrogens exchange on the ^1H NMR time scale at room temperature and appear as an averaged resonance. In contrast to other α- and β-aminoimines[8,21] it is very stable and crystalline compound, which does not decompose even when stored in air.

CONCLUSION

A variety of 1,9-disubstituted phenalenes have been synthesised which retain the geometric and specific electronic properties of the parent conjugated polycycle. One class involves a very strong hydrogen bridge protecting functional groups normally considered as sensitive combinations. The second class involves the development of a phenalenium system which stabilises valuable intermediates for the new synthetic pathways leading to the preparations of derivatives analogous to the N- and S-substituted acetylacetones. The hydrogen bridge in the appropriate molecules can be removed for the formation of stable transition metal chelate complexes.[22]

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