(6) M. J. Strauss and R. R. Bard, *J. Org. Chem.*, **43**, 3600 (1978).
(7) M. J. Strauss, D. C. Palmer, and R. R. Bard, *J. Org. Chem.*, **43**, 2041 (1978).
(8) R. G. W. Spickett and G. M. Timmis, *J. Chem. Soc.*, 2887 (1954).
(9) I. J. Pachter and P. E. Nemeth, *J. Org. Chem.*, **28**, 1187 (1963).
(10) I. J. Pachter, P. E. Nemeth, and A. J. Villani, *J. Org. Chem.*, **28**, 1197 (1963).
(11) J. Weinstock, R. Y. Dunoff, and J. G. Williams, *J. Med. Chem.*, **11**, 542 (1968).
(12) J. Weinstock, R. Y. Dunoff, B. Sutton, B. Trost, J. Kirkpatrick, and F. Farina, *J. Med. Chem.*, **11**, 549 (1968).
(13) J. Weinstock, H. Graboyes, G. Jaffee, I. J. Pachter, K. Snader, C. B. Karash, and R. Y. Dunoff, *J. Med. Chem.*, **11**, 560 (1968).
(14) W. R. Boon, W. G. M. Jones, and G. R. Ramage, *J. Chem. Soc.*, 96 (1951).
(15) S. M. Greenberg, L. O. Ross, and R. K. Robins, *J. Org. Chem.*, **24**, 1314 (1959).
(16) H. Segal and D. Shapiro, *J. Med. Chem.*, **1**, 371 (1959).
(17) J. Weinstock, J. W. Wilson, V. D. Wiebelhaus, A. R. Maass, F. T. Brennan, and G. Sosnowski, *J. Med. Chem.*, **11**, 573 (1968).

1,9-Disubstituted Phenalenes. 4.[1] Preparation and Properties of 1,9-Dihetero-Substituted Phenalenyl Cations

K. D. Franz[2]

Research School of Chemistry, Australian National University, Canberra, A.C.T., Australia 2600

Received November 22, 1978

The synthesis of new 1,9-dihetero-substituted (OR, SR, NR_2) phenalenes and phenalenyl cations is reported and their ^1H and ^{13}C NMR and UV/Vis spectra together with their redox potentials are discussed. Shifts of the ^{13}C resonances of the ring atoms of the cations indicate a close relationship with the parent compound phenalenyl. This can also be seen from the existence of the free radical and the anionic species, which can be generated electrochemically.

The odd alternant hydrocarbon phenalenyl and some of its 1-substituted derivatives are known to exist in three different oxidation states: plus, zero, minus.[3] Recently Haddon pointed out the prospect of intermolecular charge transfer in solids of carbon-centered free radicals and of phenalenyl in particular.[4] Since the parent compound is rather unstable toward dimerisation,[5] the influence of hetero substituents on the redox properties of the carbon skeleton should be of interest. 1- and 1,3-substituted derivatives are not well suited for this kind of investigation because they are either rather reactive, as in the case of 1-phenalenes,[3a,c] or may behave more like 1,8-trimethinecyanine-bridged naphthalenes.[3b,d,6] Only 1,9 substitution allows conjugation over the carbon skeleton as a whole.[3d]

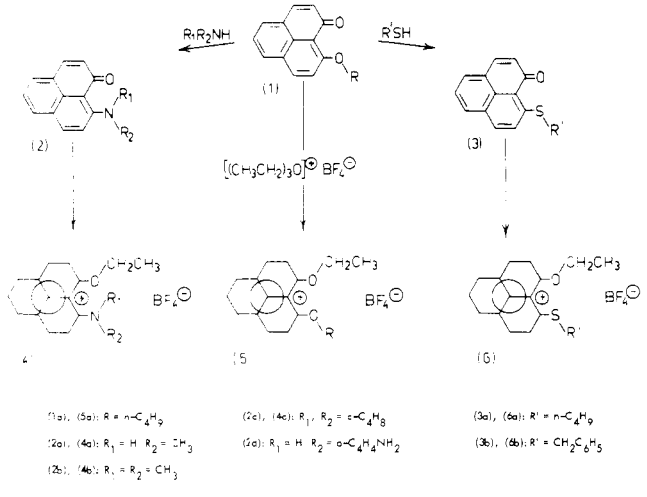
In preceding papers of this series we reported synthetic methods for the preparation of a variety of 1,9-dihetero-substituted phenalene derivatives.[7] As important intermediates in this chemistry, 1,9-disubstituted phenalenium ions have been found to be very stable cations, thus showing the same behavior as their parent compound phenalenyl.[8] Earlier results already showed that phenalenium ions have very low and reversible redox potentials, thus representing quite a unique class of nearly planar carbon-based free radicals,[8b] in contrast to other reduction products of carbonium ions which easily tend to dimerize, as for instance tropylium ions.[9] We therefore decided to further investigate the charge distribution and redox properties of 1,9-dihetero-substituted phenalenium ions.

Results

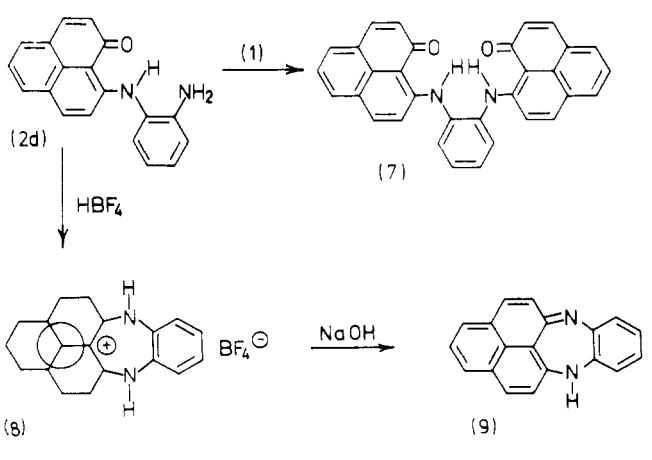
In a general reaction 9-hetero-substituted 1-phenalenones can be alkylated at the oxygen on 1 position by Meerwein's salt (Scheme I). Thus 9-butoxy-1-phenalenone (**1a**) and its N (**2**), and S (**3**) derivatives form 1,9-disubstituted phenalenium tetrafluoroborates (**4–6**).

Nucleophilic substitution of the alkoxy group by primary amines gives 9-amino-1-phenalenones (**2a,b**), in which a second substitution is normally prevented by the strong intramolecular hydrogen bond.[7] It is therefore possible to react **1** with *o*-phenylenediamine to give **2d.** At higher temperature **2d** reacts with a further molecule of **1** to form **7** (Scheme II).[10] However, in the presence of acid and above 120 °C, the internal cyclization of the diamine occurs preferentially to give 8. Treatment of the 1,5-diazepinium ion (8) with aqueous

Scheme I

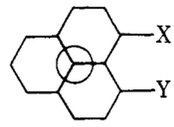


Scheme II



0022-3263/79/1944-1704$01.00/0

Table I. Electrochemical Halfwave Potentials and Electronic Absorptions of 1,9-Disubstituted Phenalenes[b,c]



no.	X	Y	registry no.	mp, °C	$E_{1/2}$[c], V	UV–vis, nm ($\epsilon \times 10^{-3}$)
1a	O	O-*n*-C_4H_9	69454-53-1		−1.12	395 (5.1), 343 (10.9), 259 (12.8)
2a	O	$HNCH_3$	69454-54-2		−1.27	474 (21.0), 349 (35.1), 254 (35.2)
2b	O	$N(CH_3)_2$	69454-55-3		−1.03	460 (8.4), 357 (13.4), 280 (17.4)
2c	O	c-NC_4H_8	69454-56-4	139	−1.44	546 (6.37), 432 (6.93), 371 (14.40), 239 (14.96)
2d	O	HN-*o*-$C_6H_4NH_2$	69454-57-5	127	−1.17	
3a	O	S-*n*-C_4H_9	69454-58-6	99	−0.96	440 (6.15), 431 (7.14), 366 (19.4)
3b	O	S-$CH_2C_6H_5$	69454-59-7		−1.25	
7			69454-60-0	275	−1.07, −1.15	462 (14.43), 443 (17.36), 355 (22.98), 277 (22.25)
4a	OCH_2CH_3	$HNCH_3$	69461-11-6		−0.39, −1.29	472 (15.7), 447 (15.0), 378 (23.8), 248 (21.8)
4b	OCH_2CH_3	$N(CH_3)_2$	69461-13-8	149	−0.35, −1.15	450 (10.17), 393 (14.68), 251 (20.72)
4c	OCH_2CH_3	*c*-NC_4H_8	69461-15-0	158	−0.43, −1.19	464 (18.43), 352 (23.54), 256 (44.34)
5a	OCH_2CH_3	O-*n*-C_4H_9	69461-17-2		−0.07, −1.11	457 (11.19), 431 (11.47), 371 (27.76), 261 (10.76)
6a	OCH_2CH_3	S-*n*-C_4H_9	69461-19-4	215	+0.06, −0.96	505 (3.61), 406 (13.54), 350 (8.13), 283 (18.06)
6b	OCH_2CH_3	$SCH_2C_6H_5$	69461-21-8	211	+0.10, −0.97	406 (7.56), 368 (9.82), 283 (18.15), 275 (15.12)
8	*o*-HNC_6H_4NH		69461-23-0	266 (dec)	−0.20, −1.22	510 (1.43), 370 (8.42), 285 (31.65)
11b	$HNCH_3$	$N(CH_3)_2$	69461-25-2		−0.43, −1.30[a]	491 (4.66), 467 (4.25), 382 (9.31), 261 (19.23)
12a	$CH_3NCH_2NCH_3$		69461-27-4	236	−0.44, −1.29[a]	535 (5.63), 387 (29.18), 259 (30.18)

[a] Irreversible. [b] Satisfactory analytical values (±0.3% for C, H, N or S, B, and F) were reported for compounds **2c,d, 3a, 4b,c, 6a,b, 7–9, 10b; 11a; 12a.** [c] The neutral compounds have been measured in acetone ($E_{1/2}$) and cyclohexane, and the cations (**4a–12a**) have been measured in acetonitrile and methylene chloride.

NaOH provides the conjugate base (**9**). Phenalenium ions of the type **4, 6,** and **8** are also accessible from **5,** but in lower yields.[11]

The formation of stable phenalenium ions is not restricted to 1-phenalenone derivatives. Protonation and alkylation also take place on 9-(methylamino)-1-methyliminophenalene (**10a**), yielding quantitatively **10b** and **11** (Scheme III). In a preceding communication we have already discussed the further oxidative cyclization of **11** to **12** and are giving here the experimental details.[1]

A common feature of the phenalene derivatives is their stability toward reduction. The electrochemical data are listed in Table I, measured by CV and ACV as shown for **6a** in Figure 1.

Neutral phenalenes (**1–3**) show one reversible reduction while **7,** with two 13-rings linked together, takes up two electrons. The phenalenium ions **4–6** and **8** generally undergo two reversible reductions.

The compounds absorb in the visible and UV region with extinction coefficients of the order of 10^4 (Table I).

Depending on substituents the ring protons appear at δ 6.5–8.2 (Table II) in the neutral phenalenones and are shifted to lower field in the cations.

Assignment of the ^{13}C resonances is possible by combination of the following results and observations: (i) proton and nonproton bonded carbon nucleii are distinguishable by the use of $Cr(acac)_3$ as relaxation agent; (ii) the shifts of C_1 and C_9 show the largest substituent effects; (iii) separation of corresponding ^{13}C signals, like those of C_2–C_8 and C_{3a}–C_{6a}, of compounds with differently substituted 1,9 positions decreases with the distance from those as can be seen for **4c** in

Scheme III

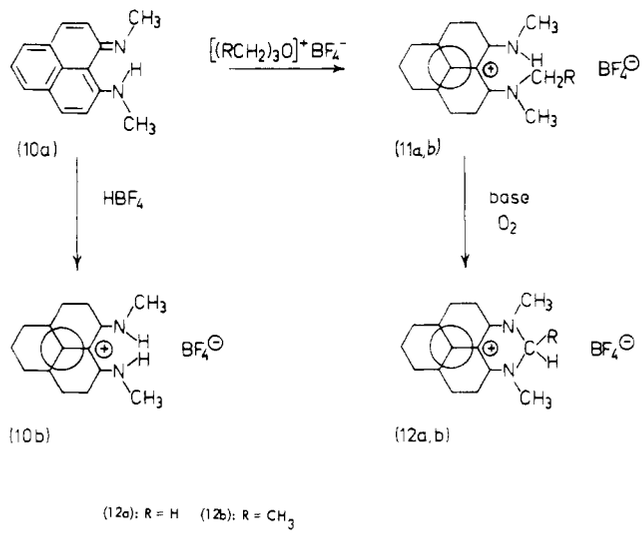


Table II. ^1H (upper row) and ^{13}C (lower row) NMR Shifts for 1,9-Disubstituted Phenalenes and Phenalene Cations[c]

	1	2	3	4	5	6	7	8	9	3a	6a	9a	9b	X/Y
1a					(6.6–7.9)[a]									4.2, 1.9, 1.6, 1.0[b]
	184.4	123.9	139.0	131.4	130.6	131.4	137.4	114.8	162.8	127.0	126.5	128.8	115.6	14.8, 65.2
2a					(6.9–7.8)[a]									3.1 (CH_3), 11.9 (NH)
	183.9	121.6	138.2	131.2	128.6	131.2	138.2	113.8	156.4	124.7	123.9	127.8	107.8	29.3
2b					(7.2–8.1)[a]									3.1
	181.4	121.9	137.4	130.5	130.3	130.3	135.1	118.3	155.3	126.0	125.1	129.7	111.4	43.6
2c					(6.8–7.9)[a]									3.4, 2.0
	181.2	121.4	137.0	130.3	130.1	129.9	134.7	117.8	152.1	125.8	124.8	129.5	111.1	25.6, 52.3
2d					(6.5–8.2)[a]									3.9 (NH_2), 13.9 (NH)
3a					(6.8–8.0)[a]									3.0, 1.7 (CH_2CH_2),
	184.8	124.9	139.3	131.3	128.9	131.1	133.5	123.6	151.8	127.8	126.6	128.4	123.9	31.8, 30.1, 22.6, 13.9
3b					(6.8–8.0)[a]									4.2 (CH_2)
7					(7.0–8.1)[a]									12.6 (NH)
4a					(7.0–8.2)[a]									4.3, 1.6/3.3, 9.9 (NH)
	167.9	117.5	146.1	138.9	127.9	137.9	144.1	116.5	162.4	127.0	126.5	127.4	109.1	70.1, 15.3/33.4
4b					(7.5–8.6)[a]									4.6, 1.6/3.7, 3.3
	165.5	120.7	143.0	136.5	126.9	136.2	142.1	116.5	164.4	128.3	127.7	128.1	109.6	–/48.5, 45.9
4c					(7.4–8.6)[a]									4.8, 1.6/4.1, 3.5, 2.3, 2.0
	164.3	119.6	141.7	135.2	125.4	134.8	141.0	115.2	159.7	126.2	126.0	126.5	109.1	67.1, 14.7/57.3, 53.8, 26.0, 24.3
5a					(7.6–8.7)[a]									4.8, 1.6/4.2, 2.6, 1.7, 1.1
	175.5	118.5	150.9	143.6	128.5	143.6	150.9	118.5	175.5	127.2	127.2	126.3	112.3	70.7, 15.0
6a					(7.8–8.9)[a]									4.9, 1.8/3.2, 2.1, 1.6, 1.0
	173.7	129.2	150.5	143.2	142.7	143.2	150.5	127.4	171.9	127.6	127.6	129.7	125.3	72.2, 15.3/35.3, 30.4, 23.2, 14.3
6b					(7.4–8.8)[a]									4.8, 1.6/4.6
8					(6.0–7.8)[a]									7.0 (NH)
11a					(7.1–8.1)[a]									3.1, 3.3 (NCH_3)
12a					(7.2–8.3)[a]									5.2 (CH_2), 3.3
	152.5	117.0	144.2	137.0	126.6	126.6	137.0	144.2	117.0	152.5	126.6	125.7	106.4	69.9, 38.3 (CH_3)

[a] Multiplett for the ^1H of the ring. [b] X = Y = CH_2CH_3. [c] At 310 K, shifts in δ for ^1H and in ppm for ^{13}C, vs. Me_4Si; BF_4^- salts in CD_3CN, others in $CDCl_3$; X and Y as in Table I.

Figure 2; (iv) the average shift per carbon of the cations relative to the neutral nonalkylated compounds indicates a deshielding of the ring positions; (v) the amount of available data is self-consistent and agrees with results from MO calculations.[12]

Experimental Section

Compounds **1a, 2a, 2b, 4a, 5a,** and **10a** have already been described.[7,14] ^1H-NMR spectra were recorded on a JEOL-Minimar 100 MHz, ^{13}C NMR spectra on a JEOL FX-60 instrument (Table II). Electrochemical data have been obtained on a three-electrode PAR Model 170 instrument with Pt working and auxiliary electrode vs. Ag/AgCl reference electrode and TEAP as supporting electrolyte (Table I). The UV–vis spectra were recorded on a Cary-14. The compounds give satisfactory microanalytical results and show parent ions in their mass spectra.

9-(Butylthio)-1-phenalenone (3a). 9-Butoxy-1-phenalenone (**1a,** 2.5 g, 10 mM) and 1 g (11 mM) of 1-butanethiol are dissolved in 70 mL of $CHCl_3$ and refluxed for 2 h. The solvent is removed under reduced pressure and the yellow residue is recrystallized from 250 mL of heptane, yielding 2.45 g (92%) of bright yellow crystals of **3a,** mp 99 °C.

The above procedure is general for the nucleophilic substitution of the 9-alkoxy group of 1 by amines and thiols: **2c,** from toluene (94%), mp 139 °C; **2d,** from heptane (86%), mp 127 °C; **3b,** from toluene (78%), mp 197 °C.

1-Ethoxy-9-(benzylthio)phenalenium Tetrafluoroborate (6b). A solution of 2.1 g (11 mM) of $(CH_3CH_2)_3O^+BF_4^-$ in 50 mL of CH_2Cl_2

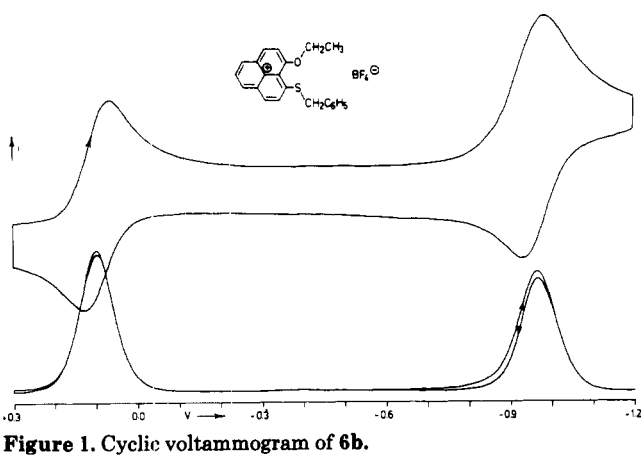


Figure 1. Cyclic voltammogram of **6b.**

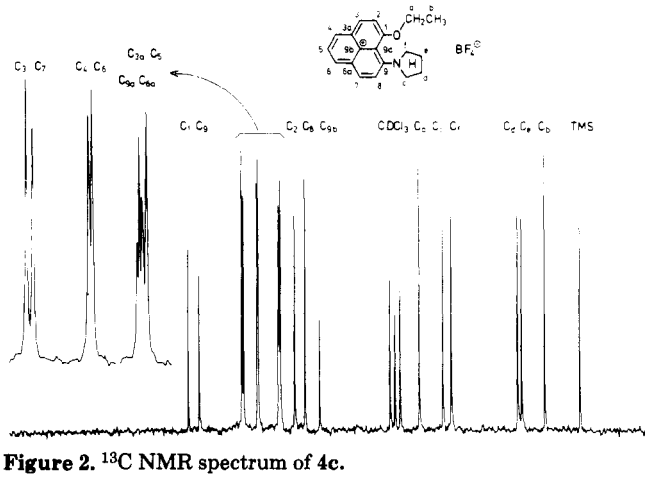


Figure 2. ^{13}C NMR spectrum of **4c.**

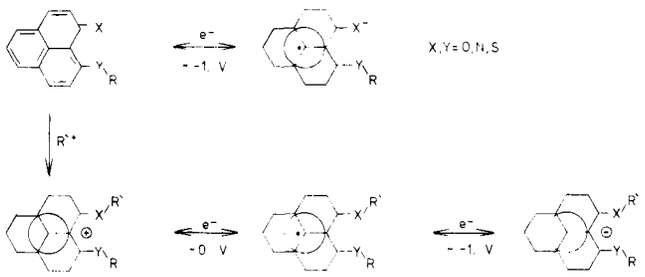


Figure 3. Relationship between the oxidation states of 1,9-disubstituted phenalenes.

is slowly added under nitrogen to 3 g (10 mM) of 9-(benzylthio)-1-phenalenone (**3b**) dissolved in 100 mL of CH_2Cl_2. After stirring the brick red solution for a further hour the solvent is removed and the residue is recrystallized from 100 mL of 3:1 CH_2Cl_2/heptane, yielding 4.2 g (89%) (6b), mp 211 °C.

The above procedure is general for the alkylation of 9-substituted 1-phenalenones: **4b,** mp 149 °C and **4c,** mp, 158 °C from 3:1 $CHCl_3$/heptane (70–75%); **6a,** mp 215 °C from 3:1 CH_2Cl_2/heptane (81%).

1,2-Bis(9'-amino-1'-phenaleno)benzene 7. 1a (14 g, 56 mM) and 3 g (28 mM) of 1,2-diaminobenzene are refluxed for 2 h in xylene. After evaporation of the solvent the residue is recrystallized from $CHCl_3$, yielding 11.5 g (89%) of **7,** mp 275 °C. The compound can also be made by starting from equimolar amounts of **1a** and **2d.**

1,2-(1',9'-Diaminophenalenium)benzene Tetrafluoroborate (8). 1a (1.4 g, 5.6 mM), 0.6 g (5.6 mM) of 1,2-diaminobenzene, and 0.5 mL of HBF_4 (40% aqueous) are refluxed in xylene for 4 h. **8** (1.62 g, 83%), mp 266 °C dec, can be isolated after concentrating and cooling the solution.

1,2-(9'-Amino-1'-phenalenimino)benzene (9). 8 (0.36 g, 1 mM) is suspended in 50 mL of toluene and slowly treated with 10 mL of aqueous NaOH (0.25 N). Separation, drying, and concentration of the dark red solution gives 0.24 g (89%) of grayish powdered **9,** mp 195 °C.

1,9-Bis(methylamino)phenalenium Tetrafluoroborate (10b). HBF_4 (2 mL, 40% aqueous) is slowly added to 2.2 g (10 mM) of **10a** dissolved in 50 mL of CH_3OH. Within 10 min **10b** precipitates quantitatively as a red powder, which can be recrystallized from $CHCl_3/CH_3CN$, mp 213 °C.

9-(Dimethylamino)-1-(methylamino)phenalenium Tetrafluoroborate (11a). $[(CH_3)_3O]^+BF_4^-$ (0.7 g, 47 mM) dissolved in 20 mL of CH_2Cl_2 is added to 1 g (45 mM) of **10a** in 50 mL of CH_2Cl_2 and stirred for 1 h. Concentration of the solution yields 1.3 g of **11a,** mp 213 °C. The analogous procedure with $[(CH_3CH_2)_3O]^+BF_4^-$ gives **11b,** mp 203 °C.

1,3-Dimethyl-1,3-diaza-2*H*-pyrenium Tetrafluoroborate (12a). A solution of 1 g (31 mM) of **11a** in 20 mL of CH_3CN is treated with 10 mL of $(CH_3)_2NH$ (30% ethanolic solution) for 20 min in an open beaker. After the addition of 50 mL of heptane 0.6 g of a purple precipitate is formed which can be recrystallized from $CHCl_3/CH_3CN$, mp 223 °C. The analogous procedure starting from **11b** gives **12b,** mp 236 °C.

Discussion

Perturbation by substituents at the 1 and 9 positions does not alter the interesting behavior of these phenalene derivatives, namely to be stable in up to three oxidation states like their parent compound phenalenyl. Neutral phenalenones and phenalenethiones show only one reduction,[7] and have to be oxidized by alkylation. With two singly bonded substituents on the 1,9 position delocalization of the additional electrons takes place over the whole π system (Figure 3).

Reduction of the neutral compounds occurs at about −1.0 V and is influenced by the 9-substituents. The higher inductive effect of the pyrrolidine group in **2d** compared to the dimethylamino group in **2b** shows up in the increased reduction potential. The more negative potential required for **2a** in relation to **2b** may be due to the additional energy necessary to overcome the hydrogen bridge. Linking together two phenalenones by 1,2-diaminobenzene (**7**) results only in a weak coupling of the two systems, as can be seen by the small shift and difference of the two redox potentials.

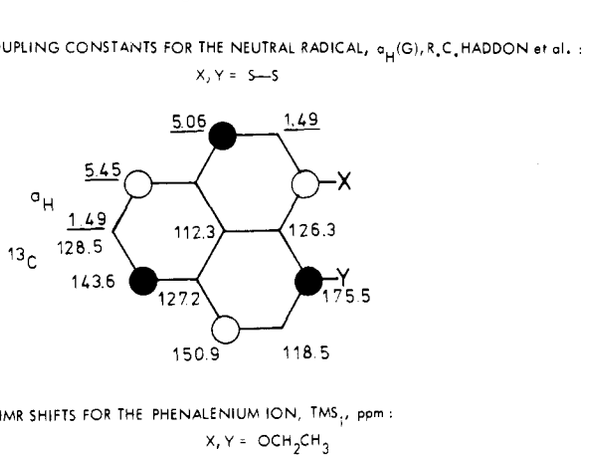


Figure 4. Nodal properties of the phenalenyl frontier orbital; the EPR coupling constants are underlined.

The redox processes must take place on the carbon skeleton, since at least all of the first reductions are completely reversible, even in cases where a loss of hydrogen would be probable, as for instance in **2a, 4a, 8, 11a,b,** and **12a,b.** Even in the very unfavorable case of phenaleno[1,9-*c,d*]dithiolyl about 80% of the spin density is located on the phenalenyl ring,[8b] although the disulfide bridge can be regarded as an enlargement of the conjugated system.

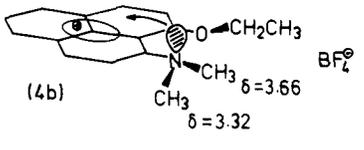
The frontier orbital, which is a nonbonding orbital of phenalenyl, is mainly located on $C_{1,3,4,6,7,9}$, thus demonstrating the ambiguity of the "obvious" formula with localized double bonds.[4,15] This seems to be also true for the 1,9-disubstituted derivatives.

The major localization of the positive charge in the cations is indicated by the positions of the ^{13}C resonances and their shifts compared to the nonalkylated parent compounds (Table II). Except for C_1, which changes the type of its substituent, all the above mentioned positions ($C_{1,3,4,6,7,9}$) are shifted to lower field, while the rest remain nearly constant. Those hydrogens show the largest hyperfine splitting constant in the free radical,[8c] which are attached to carbons with low-field resonances in the ^{13}C NMR spectra of the phenalenium ions (Figure 4).

1,9-Disubstituted phenalenium cations show typically two reversible reductions, the first step ranging from +0.1 to −0.44 V and the second step closer together within the different compounds around −1.1 V. These low values quite clearly indicate the close relationship with the parent compound. The stabilities of the three oxidation states are independent of the geometry and electronic nature of many substituents, thus demonstrating the existence of a new class of multiple redox active compounds.

Within the O-alkylated cations the 9-amino compounds have significantly higher first reduction potentials than the O and S derivatives. This can be understood by looking at the ^1H and ^{13}C NMR spectra, where two and four signals appear for the nuclei of the 9-substituents of **4b** and **4c,** as can be seen in Figure 2 and Table II.

It is therefore likely that the C_9–N bond is in part a double bond. Because of the steric effect of the 1-substituent, OR, a tilted structure, as indicated for **4b,** seems to be favorable. The



degree of planarity will determine the amount of positive charge on the nitrogen. The stabilizing effect of the amino group[16] shows up in the increased first reduction potentials

of these cations and in the position of the magnetic resonances of the hydrogen and carbon nuclei belonging to the ring.

With this above described new class of compounds, a promising type of organic cations, whose steric and electronic properties are quite variable, has been found. In view of their low first redox potentials they are interesting counterions in charge-transfer salts with organic or inorganic anions, for instance with $TCNQ^-$ or bis(dithiolato)–metal complex anions.[17]

Acknowledgment. I am grateful to Mrs. J. Hope for assistance with the electrochemical measurements and Professor R. L. Martin for helpful discussions.

Registry No.—**9**, 68057-87-4; **10a**, 67618-28-4; **10b**, 69461-29-6; **11b**, 69461-31-0; **12b**, 69470-08-2; 1,2-diaminobenzene, 95-54-5.

References and Notes

(1) Part 3. K. D. Franz, *Chem. Lett.*, submitted for publication; parts of this paper have been presented at the Australian Conference on Coordination and Organometallic Chemistry, Melbourne, February 1977.
(2) IBM T. J. Watson Research Center, P. O. Box 218, Yorktown Heights, New York 10598.
(3) (a) P. Beckmann, *Aust. J. Chem.*, **14**, 229 (1961); (b) S. Huenig and E. Wolf, *Chimia*, **22**, 33 (1968); (c) C. Jutz, R. Kirchlechner, and H. J. Seidel, *Chem. Ber.*, **102**, 2301 (1969); (d) J. Fabian, *J. Prakt. Chem.*, **320**, 361 (1978).
(4) R. C. Haddon, *Nature (London)*, **256**, 394 (1975).
(5) F. Gerson, E. Heilbronner, H. A. Reddock, D. H. Paskovich, and N. C. Das, *Helv. Chim. Acta*, **50**, 813 (1967).
(6) S. Huenig and E. Wolf, *Justus Liebigs Ann. Chem.*, **732**, 7 (1970); **732**, 26 (1970).
(7) K. D. Franz and R. L. Martin, *Tetrahedron*, **34**, 2147 (1978).
(8) While this work was in progress two other types of 1,9-disubstituted phenalenium ions have been reported: (a) K. Yamamoto, Y. Kayane, and I. Murata, *Bull. Chem. Soc. Jpn.*, **50**, 1964 (1977); (b) R. C. Haddon, F. Wudl, M. L. Kaplan, J. H. Marshall, and F. B. Bramwell, *J. Chem. Soc., Chem. Commun.*, 429 (1978); (c) R. C. Haddon, F. Wudl, M. L. Kaplan, and F. B. Bramwell, *J. Am. Chem. Soc.*, **100**, 7629 (1978).
(9) J. M. Leal, T. Teherani, and A. J. Bard, *J. Electroanal. Chem.*, **91**, 275 (1978).
(10) Typically, β-hydroxy ketones and their derivatives cyclize with 1,2-diaminobenzene in the absence of metal ions to 1,5-diazepines: F. D. Popp and A. Catala Noble, *Adv. Heterocycl. Chem.*, **8**, 66 (1967).
(11) This approach has been used by Neidlein and Behzadi for **4b** and **8** independently from our investigations: R. Neidlein and Z. Behzadi, *Chem. Ztg.*, **102**, 199 (1978).
(12) F. Carnovale, T. H. Gan, J. B. Peel, and K. D. Franz, *Tetrahedron*, submitted for publication. There is a good correlation between calculated and assigned values for this class of compounds, although correspondence of charge density and ^{13}C NMR shifts is generally unreliable.[13]
(13) G. L. Nelson and E. A. Williams, *Prog. Phys. Org. Chem.*, **12**, 229 (1976).
(14) K. D. Franz and R. C. Haddon, *Org. Prep. Proced. Int.*, submitted for publication.
(15) I. Murata, *Top. Nonbenzoic Arom. Chem.*, **1**, 159 (1976).
(16) This effect has been also shown for dialkylaminotropylium ions: H. Froehlisch and R. Braun, *Tetrahedron Lett.*, 2735 (1978).
(17) K. D. Franz, submitted for publication.

Fluoroalkanesulfonyl Chlorides

George G. I. Moore

Riker Laboratories, Inc., 3M Center, St. Paul, Minnesota 55101

Received November 3, 1978

A simple and effective synthesis of CH_2FSO_2Cl and CHF_2SO_2Cl has been achieved, both in 49% overall yield. The (di)fluoromethyl chlorides are converted into the (di)fluoromethyl benzyl sulfides by NaOH–benzyl mercaptan in DMF. Oxidative chlorination in cold water yields the (di)fluoromethanesulfonyl chlorides.

$$CH_xF_yCl \xrightarrow[DMF]{PhCH_2SNa} CH_xF_ySCH_2Ph \xrightarrow[H_2O]{Cl_2} CH_xF_ySO_2Cl$$

$x = 1, y = 2$

$x = 2, y = 1$

Despite identical conditions and yields, the reactions of benzyl mercaptide with CH_2FCl and CHF_2Cl proceed through S_N2 and carbene paths, respectively, as indicated by alkylation in NaOD. The oxidative chlorination of CHF_2SCH_2Ph occurs at least 50% via the sulfoxide. In situ generation of benzyl mercaptide gave a 39% overall yield of CHF_2SO_2Cl. *tert*-Butyl mercaptan proved inferior in the difluoromethylation step.

Our interest in the biological properties of various fluoroalkanesulfonamides (to date, antiinflammatory,[1] anticonvulsant,[2] cardiovascular,[3] and herbicidal[4]) has necessitated large-scale preparations of CH_2FSO_2Cl (**1**) and CHF_2SO_2Cl (**2**). Farrar's[5] original synthetic route to **2** consisted of the Strecker sequence shown in eq 1. After considerable modification, Harrington and Kaufman[6] rendered this adequate for small-scale preparations (<500 g, yields ~50%), but this route has proven complicated and inefficient (10–20% yields) for larger runs, unreliable, and hence too expensive for multigallon reactions. Specifically, the initial step required extended heating in a high-pressure kettle, resulting in extensive corrosion of the vessel. Yields in this step were particularly erratic for CHF_2Cl (several <10%). Recovery and purification of the sulfonate salts were time consuming. The final mixture of **2** (bp 96 °C) and byproduct $POCl_3$ (bp 101 °C) could not be separated by distillation, and only by competitive hydrolysis could the latter be removed. The **2** so obtained was contaminated with 5–15% of unidentified materials.

$$CH_2FCl + Na_2SO_3 \xrightarrow[\text{pressure}]{\Delta} CH_2FSO_3Na \xrightarrow{PCl_5} \underset{\mathbf{1}}{CH_2FSO_2Cl} \quad (1)$$

$$CHF_2Cl + Na_2SO_3 \rightarrow CHF_2SO_3Na \rightarrow \underset{\mathbf{2}}{CHF_2SO_2Cl} \quad (2)$$

We decided to employ the greater nucleophilicity of divalent sulfur by (di)fluoromethylating some species RSH, followed by cleavage of the protecting group R and oxidation to the tetravalent state, in either order. This approach was designed to avoid both the slow, corrosive pressure reaction with Na_2SO_3 and the difficult isolation of the sodium sulfonates. Our efforts culminated in the synthesis of benzyl sulfides **3** and **4** and subsequent direct conversion of these to **1** and **2** by cold aqueous chlorination.

0022-3263/79/1944-1708$01.00/0