# An Electron Spin Resonance Investigation of the Products of the Friedel–Crafts Reaction of Sulphur Dioxide with Methylnaphthalenes

**Martin G. Bakker, Rodney F. C. Claridge,* and Christopher M. Kirk**
*Department of Chemistry, University of Canterbury, Private Bag, Christchurch, New Zealand*

A series of mono-, di-, tri-, tetra-, and hexa-methylnaphthalenes, and naphthalene were reacted with $AlCl_3$–$SO_2$, $AlCl_3$–$SOCl_2$, or $AlCl_3$–$S_2Cl_2$, using $CH_2Cl_2$ as solvent. The radical cation products produced were studied using e.s.r. 1,4-, 1,5-, and 1,8-dimethyl-, 1,2,4-trimethyl-, 1,2,3,4- and 1,3,5,7-tetramethyl-, 1,2,3,4,5,8-hexamethyl-, and octamethyl-naphthalene all gave predominantly spectra from the monomer cation radical. Naphthalene, 1- and 2-methyl- and 1,3-, 1,6-, 1,7-, 2,3-, 2,6-, and 2,7-dimethylnaphthalene gave predominantly spectra ascribed to methyl derivatives of naphtho[1,8-*cd*]-1,2-dithiole. Spectra from these compounds also contained a significant component which was ascribed to methylperylenes formed from the Scholl condensation of the parent compound. A species described as 3*H*,10*H*-acenaphtho[1,2-*c*]-1,2-dithiete was observed as a minor product in the reactions with 1,8-dimethylnaphthalene.

The interest shown by e.s.r. spectroscopists in the anions formed from naphthalene and its methyl derivatives[1–6] has not been matched by a similar interest in the cations. The additivity relationship for the methylnaphthalene anions has been determined with some precision[3,7] whereas insufficient coupling constants are known to allow the determination of an additivity relationship for cations. Our particular interest was in determining if the absence of perturbing effects, such as the ion-pairing, observed in the methylnaphthalene anions, would result in better agreement between the additivity relationship and the observed coupling constants of methylnaphthalene cations.

The first study of methylnaphthalene cation radicals was the formation of naphthalene dimer cation by reaction with $SbCl_5$ in $CH_2Cl_2$ reported by Lewis and Singer.[8] Howarth and Fraenkel[9] reported the monomer cation of 1,4,5,8-tetramethylnaphthalene and the dimer of 2,3,6,7-tetramethylnaphthalene. Root and Rogers[10] using sulphuric acid observed the e.s.r. spectra of octamethyl- and 1,2,3,4,5,8- and 1,2,3,4,6,7-hexamethyl-naphthalene monomer cation radicals. Yoshimi and Kuwata[11] used $SbCl_5$ in a mixture of $CH_2Cl_2$ and $SO_2$ to oxidise 1,4-, 1,5-, and 1,8-dimethylnaphthalene. These authors reported the formation of the monomer cation from all three and also observed a dimer spectrum from 1,4-dimethylnaphthalene. The only other report of an e.s.r. spectrum from a methylnaphthalene cation is that of Gerson *et al.*[4] who oxidised 1,2,3,4-tetramethylnaphthalene with $AlCl_3$ in $CH_3Cl$.

$AlCl_3$ has proved to be a particularly good oxidising agent for e.s.r. studies.[12] Our own experience[13,14] has shown that the $AlCl_3$–$SO_2$ couple is particularly suitable for oxidising various naphthalene derivatives to form identifiable radical cations.

We had anticipated observing some by-products from the Scholl condensation,[15] but were not expecting the diversity of reaction products which were observed.

## Experimental

The e.s.r. spectra were collected on a Varian E-12 spectrometer using a microcomputer-based data acquisition system. A Varian V4557 temperature controller was used to regulate the temperature. Perylene anion in dimethoxyethane was used as the standard for *g* value measurements.

The aluminium trichloride used was triply sublimed under vacuum, *in situ* through glass wool. Standard preparative techniques for formation of the radical cations were used.

Unless indicated all splitting constants were refined using a modified form of program ESRCON.[16]

The observations and spectra from the reactions of naphthalene will be described in detail. The spectra of the other compounds studied can be assumed to have given similar results if no comment to the contrary is made.

On contact with the sublimed aluminium trichloride the naphthalene formed a pale pink adduct. Addition of solvent dichloromethane by distillation in vacuum gave a solution of the olive green colour characteristic of naphthalene ions. On addition of sulphur dioxide the solution became a pale brown. The observed e.s.r. spectrum is given in the Figure, and is a composite of contributions from several species. Two of the species gave spectra with linewidths *ca.* 0.1 G, centred at $g = 2.008$ and 2.003. A third species gave a single broad line of linewidth 15—20 G centred at $g = 2.004$. The precise ratio of intensities of the three species varied from sample to sample, and was not strongly influenced by the proportions of the reagents used. Replacement of $SO_2$ by $SOCl_2$ or $S_2Cl_2$ gave similar reactions. Repeated attempts with $SCl_2$ failed to give any e.s.r. spectra.

## Results and Discussion

The type of the possible species characterised are summarised in Table 1, and the observed e.s.r. parameters are given in Tables 2 and 3. A representation of the possible pathways to the observed products is shown for naphthalene in Scheme 1. The products for the methylnaphthalenes depend on the position of methyl substitution.

*Methylnaphthalene Monomer Cations.*—1,4-, 1,5-, and 1,8-dimethyl-, 1,2,3,4- and 1,3,5,7-tetramethyl-, 1,2,3,4,5,8-hexamethyl-, and octamethyl-naphthalene all formed the corresponding monomer cation radicals of the parent hydrocarbon.

A crude sample of 1,2-dimethylnaphthalene was used and a spectrum which we attribute to 1,2,4-trimethylnaphthalene monomer cation radical was observed. $^1H$ N.m.r. and h.p.l.c. both showed the presence of an impurity. The 9.89 and 8.99 G splitting constants of the observed species must be assigned to $\alpha$-methyl groups; therefore the three possible trimethylnaphthalene cation radicals are 1,2,4-, 1,2,5-, and 1,2,8-trimethylnaphthalene$^{+\bullet}$. The identification of the observed cation radical

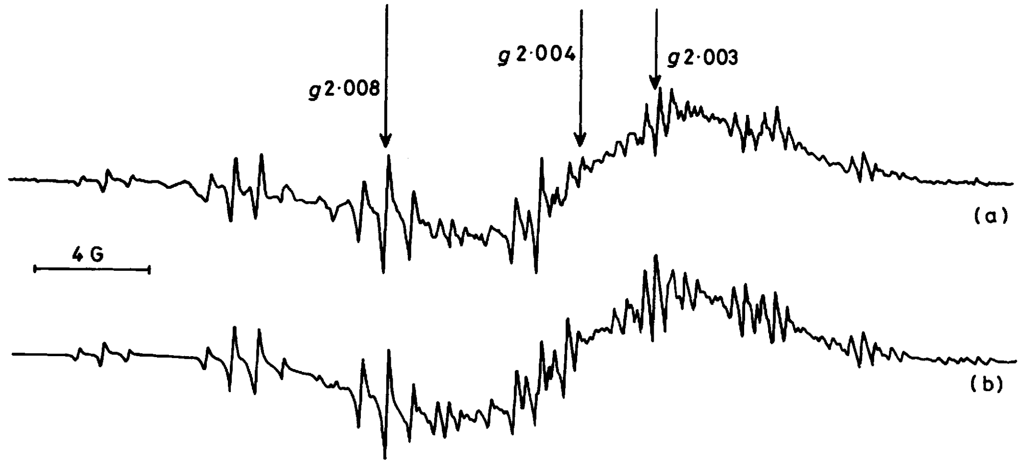


**Figure.** E.s.r. spectra from the products of the reaction of naphthalene with $AlCl_3-SO_2$ in $CH_2Cl_2$. (*a*) Experimental spectrum at −60 °C. (*b*) Simulated spectrum composed of spectra from; (1) naphthalene disulphide$^{+\bullet}$ ($g$ = 2.0083, splitting constants 5.260, 4.416, and 0.883 G, linewidth 0.15 G), (2) perylene$^{+\bullet}$ ($g$ 2.0028, splitting constants 4.033, 3.030, and 0.414 G, linewidth 0.15 G), (3) Lorentzian curve of linewidth 7 G to simulate the baseline. The relative contributions of the three component spectra are approximately equal

**Table 1.** Products of the reaction of $AlCl_3-SO_2$ with methylnaphthalenes[a]

| Compound | Monomer | Dimer | Disulphide | Perylene | Other |
|---|---|---|---|---|---|
| Naphthalene | | X | X | X | X |
| 1-MN[b] | | | X | | X |
| 2-MN | | | X | ? | X[c] |
| 1,2-DMN | | | ? | ? | X |
| 1,3-DMN | | | X | ? | |
| 1,4-DMN | X | | | | X |
| 1,5-DMN | X | | | | |
| 1,6-DMN | | | X | ? | |
| 1,7-DMN | | | X | X | |
| 1,8-DMN | X | ? | X | | X |
| 2,3-DMN | | | X | ? | |
| 2,6-DMN | | ? | X | | |
| 2,7-DMN | | | X | ? | |
| 1,2,4-TriMN | X | | | | |
| 1,2,3,4-TMN | X | | | | |
| 1,3,5,7-TMN | X | | | | |
| 1,2,3,4,5,-PentaMN | X | | | | |
| 1,2,3,4,5,8-HexaMN | X | | | | |
| OctaMN | X | | | | |

[a] X = product observed. ? = Believed to be product observed. [b] MN = methylnaphthalene, DMN = dimethylnaphthalene, TMN = tetramethylnaphthalene. [c] Observed with $SOCl_2$ only.

as 1,2,4-trimethylnaphthalene$^{+\bullet}$ is based on the application of the additivity relationship to the β-proton splitting constants of the monomer radical cations. Additivity relationships were calculated for each of the possible assignments of splitting constants for each of the three possible structures (1,2,4-, 1,2,5-, and 1,2,8-trimethylnaphthalene). The residual sum of squares of the differences between the splitting constants predicted by an additivity relationship and the measured splitting constants was used as a measure of the goodness of fit of that additivity relationship. The assignment and structure that gave the smallest residual sum of squares was chosen as the most probable structure and assignment.

The refined additivity parameters are given in Table 4. The splitting constants for 1,2,4-trimethylnaphthalene$^{+\bullet}$ were assigned by using the additivity relationship determined, where possible; otherwise assignments were made using INDO molecular orbital calculations.[17,18]

The splitting constants determined for 1,5- and 1,8-dimethylnaphthalene$^{+\bullet}$ agree reasonably well with those reported by Yoshimi and Kuwata.[11] However, our splitting constants for 1,4-dimethylnaphthalene$^{+\bullet}$ vary considerably from those reported[11] for 1,4-dimethylnaphthalene$^{+\bullet}$. Our spectra were of considerably better signal-to-noise ratio and resolution than those published by Yoshimi and Kuwata, and so we feel confident of the correctness of our results.

The agreement between our splitting constants for 1,2,3,4-tetramethylnaphthalene$^{+\bullet}$ and those reported by Gerson *et al.*[4] is satisfactory, as is that between our splitting constants for 1,2,3,4,5,8-hexa- and octamethyl-naphthalene$^{+\bullet}$ and those reported by Root and Rogers.[10]

The anomalous temperature behaviour of 1,8-di-, 1,2,3,4,5,8-hexa-, and octa-methylnaphthalene$^{+\bullet}$ has been reported previously[19] and results from hindered rotation of the α-methyl groups in these compounds.

**Table** 2. Additivity parameters for naphthalene disulphides[a]

Part A: refined additivity parameters

| Parameter | Value | Parameter | Value | Parameter | Value |
|---|---|---|---|---|---|
| $a_3$ | 4.380 ± 0.028[b] | $a_4$ | 0.874 ± 0.011 | $a_5$ | 5.203 ± 0.069 |
| | | $\Delta_{43}$ | 0.132 ± 0.009 | $\Delta_{53}$ | −0.219 ± 0.060 |
| $\Delta_{34}$ | −0.413 ± 0.030 | | | $\Delta_{54}$ | 0.169 ± 0.062 |
| $\Delta_{35}$ | −0.061 ± 0.030 | $\Delta_{45}$ | −0.284 ± 0.010 | | |
| $\Delta_{36}$ | −0.355 ± 0.030 | $\Delta_{46}$ | −0.129 ± 0.011 | $\Delta_{56}$ | −0.103 ± 0.062 |
| $\Delta_{37}$ | 0.139 ± 0.030 | $\Delta_{47}$ | 0.030 ± 0.010 | $\Delta_{57}$ | 0.231 ± 0.074 |
| $\Delta_{38}$ | −0.395 ± 0.024 | $\Delta_{48}$ | −0.239 ± 0.009 | $\Delta_{58}$ | 0.061 ± 0.060 |

Part B: observed and calculated splitting constants

| Compound | Position | $g$[c] | Equation | Expt.[d] (G) | Calc. (G) | Diff. (G) |
|---|---|---|---|---|---|---|
| NDS[e] | 3 | 2.0083 | $a_3$ | 4.416 | 4.380 | 0.036 |
| | 4 | | $a_4$ | 0.883 | 0.874 | 0.009 |
| | 5 | | $a_5$ | 5.260 | 5.203 | 0.057 |
| 3-MDS | 3 | 2.0084 | | 4.525 | | |
| | 4 | | $a_4 + \Delta_{46}$ | 0.990 | 1.006 | −0.016 |
| | 5 | | $a_5 + \Delta_{53}$ | 4.992 | 4.983 | 0.009 |
| | 6 | | $a_5 + \Delta_{58}$ | 5.140 | 5.142 | −0.002 |
| | 7 | | $a_4 + \Delta_{48}$ | 0.628 | 0.635 | −0.007 |
| | 8 | | $a_3 + \Delta_{38}$ | 3.971 | 3.986 | −0.015 |
| 5-MDS | 3 | 2.0082 | $a_3 + \Delta_{35}$ | 4.286 | 4.320 | −0.034 |
| | 4 | | $a_4 + \Delta_{35}$ | 0.588 | 0.590 | −0.002 |
| | 5 | | | 6.001 | | |
| | 6 | | $a_5 + \Delta_{56}$ | 4.978 | 5.099 | −0.121 |
| | 7 | | $a_4 + \Delta_{46}$ | 0.754 | 0.746 | 0.008 |
| | 8 | | $a_3 + \Delta_{36}$ | 4.002 | 4.025 | −0.023 |
| 3,4-DMDS | 3 | 2.0082 | | 4.302 | | |
| | 4 | | | 0.848 | | |
| | 5 | | $a_5 + \Delta_{53} + \Delta_{54}$ | 5.074 | 5.152 | −0.078 |
| | 6 | | $a_5 + \Delta_{57} + \Delta_{58}$ | 5.292 | 5.373 | −0.081 |
| | 7 | | $a_4 + \Delta_{47} + \Delta_{48}$ | 0.661 | 0.665 | −0.004 |
| | 8 | | $a_3 + \Delta_{37} + \Delta_{38}$ | 4.102 | 4.125 | −0.023 |
| 3,5-DMDS | 3 | 2.0079 | | 4.308 | | |
| | 4 | | $a_4 + \Delta_{43} + \Delta_{45}$ | 0.716 | 0.722 | −0.006 |
| | 5 | | | 5.833 | | |
| | 6 | | $a_5 + \Delta_{56} + \Delta_{58}$ | 5.107 | 5.038 | 0.069 |
| | 7 | | $a_4 + \Delta_{46} + \Delta_{48}$ | 0.495 | 0.507 | −0.012 |
| | 8 | | $a_3 + \Delta_{36} + \Delta_{38}$ | 3.655 | 3.630 | 0.025 |
| 3,6-DMDS | 3 | | | 4.044 | | |
| | 4 | | $a_4 + \Delta_{43} + \Delta_{46}$ | 0.881 | 0.878 | 0.003 |
| | 5 | | $a_5 + \Delta_{53} + \Delta_{56}$ | 4.887 | 4.880 | 0.007 |
| | 6 | | | 5.726 | | |
| | 7 | | $a_4 + \Delta_{45} + \Delta_{48}$ | 0.349 | 0.351 | −0.002 |
| | 8 | | $a_3 + \Delta_{35} + \Delta_{38}$ | 3.936 | 3.925 | 0.011 |
| 3,7-DMDS | 3 | 2.0080 | | 4.761 | | |
| | 4 | | $a_4 + \Delta_{43} + \Delta_{47}$ | 1.029 | 1.036 | −0.007 |
| | 5 | | $a_5 + \Delta_{53} + \Delta_{57}$ | 5.295 | 5.214 | 0.081 |
| | 6 | | $a_5 + \Delta_{54} + \Delta_{58}$ | 5.343 | 5.311 | 0.032 |
| | 7 | | | 0.485 | | |
| | 8 | | $a_3 + \Delta_{34} + \Delta_{38}$ | 3.574 | 3.574 | 0.002 |
| 3,8-DMDS | 3 | 2.0081 | | 4.060 | | |
| | 4 | | $a_4 + \Delta_{43} + \Delta_{48}$ | 0.793 | 0.767 | 0.026 |
| | 5 | | $a_5 + \Delta_{53} + \Delta_{58}$ | 4.904 | 4.922 | −0.018 |
| 4,6-DMDS | 3 | | $a_3 + \Delta_{34} + \Delta_{36}$ | 4.481 | 4.458 | 0.023 |
| | 4 | | | 0.631 | | |
| | 5 | | $a_5 + \Delta_{54} + \Delta_{56}$ | 5.314 | 5.268 | 0.046 |
| | 6 | | | 6.167 | | |
| | 7 | | $a_4 + \Delta_{45} + \Delta_{47}$ | 0.631 | 0.620 | 0.011 |
| | 8 | | $a_3 + \Delta_{35} + \Delta_{37}$ | 3.610 | 3.612 | −0.002 |
| 5,6-DMDS | 3 | | $a_3 + \Delta_{35} + \Delta_{36}$ | 3.85 | 3.864 | (−0.014)[f] |
| | 4 | | $a_4 + \Delta_{45} + \Delta_{46}$ | 0.45 | 0.413 | (0.037) |
| | 5 | | | 6.4 | | |

Standard deviation; parameter set:

| | |
|---|---|
| $a_3$ | 0.035 |
| $a_4$ | 0.015 |
| $a_5$ | 0.087 |

[a] The contribution to the splitting constant in position $K$ by a methyl group at position $J$ is defined $\Delta_{KJ}$, where the molecular symmetry is used to orient the molecule to minimise the value of $K$. [b] The error given is the estimate parameter standard deviation. [c] Error ±0.0002. [d] Error ±0.006 G. [e] Abbreviations used: naphthalene disulphide (NDS), methylnaphthalene disulphide (MDS), dimethylnaphthalene disulphide (DMDS). [f] Observations from this compound were not included in the determination of the additivity relationship.

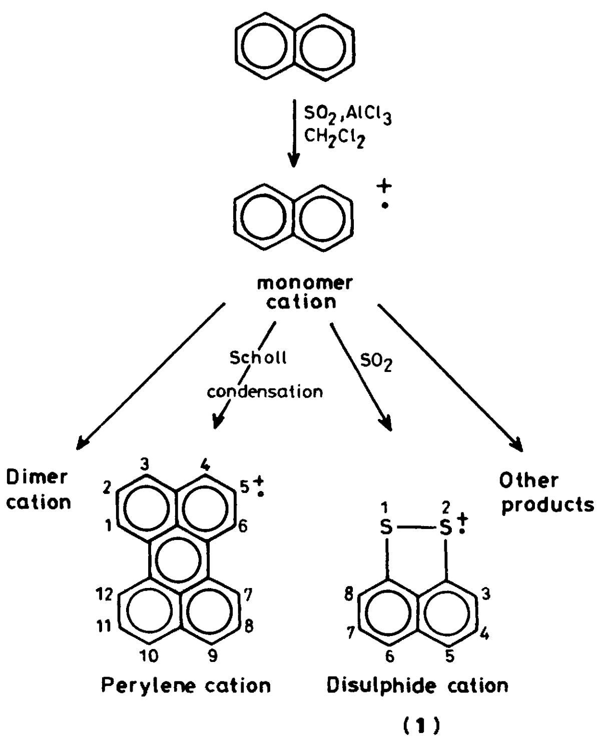
**Table 3.** E.s.r. splitting constants of radical cations of some methylnaphthalene derivatives

| Compound[a] | $T$/°C[b] | $g$[c] | Position | Splitting constant (G) | |
|---|---|---|---|---|---|
| | | | | This work[d] | Other |
| (Naphthalene) | −60 | 2.003[e] | | | |
| (1-MN) | −60 | 2.006[e] | | 4.770 (6 H)[f] | |
| | | | | 2.306 (2 H) | |
| | | | | 0.440 (4 H) | |
| | | | | 0.270 (2 H) | |
| | | | | 0.020 (2 H) | |
| (2-MMN) | −60 | 2.014[e] | | | |
| (1,2-DMN) | −60 | 2.012[e] | | | |
| 1,4-DMN$^{+\bullet}$ | −80 | 2.0027 | 1 | 9.726 | 9.63[g] |
| | | | 2 | 2.189 | 3.75 |
| | | | 5 | 3.960 | 3.84 |
| | | | 6 | 1.346 | 2.36 |
| (1,4-DMN) | −60 | 2.005[e] | | | |
| (1,4-DMN) | −60 | 2.015[e] | | | |
| 1,5-DMN$^{+\bullet}$ | −72 | 2.0029 | 1 | 7.095 | 7.07[g] |
| | | | 2 | 1.772 | 1.69 |
| | | | 3 | 1.584 | 1.69 |
| | | | 4 | 5.348 | 5.34 |
| 1,8-DMN$^{+\bullet}$ | −84 | 2.0028 | 1 | 8.305[h] | 8.25[g] |
| | | | 2 | 2.480 | 2.45 |
| | | | 3 | 1.136 | 1.16 |
| | | | 4 | 5.725 | 5.73 |
| (1,8-DMN) | −39 | 2.003[e] | | 6.5 (3 H)[f] | |
| | | | | 0.33 (4 H) | |
| (2,3-DMN) | −60 | 2.003[e] | | | |
| (2,6-DMN) | −60 | 2.0026 | | | |
| 1,2,4-TriMN$^{+\bullet}$ | −64 | 2.0027 | 1 | 9.891 | |
| | | | 2 | 3.855 | |
| | | | 3 | 0.959 | |
| | | | 4 | 8.993 | |
| | | | 5 | 3.306 | |
| | | | 6 | 2.042 | |
| | | | 7 | 0.729 | |
| | | | 8 | 4.227 | |
| 1,2,3,4-TMN$^{+\bullet}$ | −84 | 2.0030 | 1 | 9.451 | 9.36[i] |
| | | | 2 | 2.386 | 2.41 |
| | | | 5 | 3.691 | 3.71 |
| | | | 6 | 1.403 | 1.33 |
| 1,3,5,7-TMN$^{+\bullet}$ | −85 | 2.0027 | 1 | 6.450 | |
| | | | 2 | 0.068 | |
| | | | 3 | 5.042 | |
| | | | 4 | 5.078 | |
| 1,2,3,4,5,8-Hexamethylnaphthalene$^{+\bullet}$ | −90 | 2.0030 | 1 | 7.879 | 7.87[j] |
| | | | 2 | 1.938 | 1.99 |
| | | | 5 | 6.335 | 6.32 |
| | | | 6 | 1.630 | 1.55 |
| Octamethylnaphthalene$^{+\bullet}$ | −32 | | 1 | 6.54[h] | 6.45[j] |
| | | | 2 | 1.85 | 1.85 |
| Perylene$^{+\bullet}$ | −60 | | 1 | 3.030 | 3.056[k] |
| | | | 2 | 0.414 | 0.447 |
| | | | 3 | 4.033 | 4.054 |
| 2,4,9,11-Tetramethylperylene$^{+\bullet}$ | −60 | 2.003 | 4 | 6.735 (6 H)[f] | |
| | | | | 1.712 (2 H) | |
| | | | | 0.930 (2 H) | |
| | | | | 0.843 (2 H) | |
| | | | 2 | 0.326 (6 H) | |
| | | | | 0.099 (2 H) | |
| 3,9-Dimethylperylene$^{+\bullet}$ | −60 | | | 4.389 (6 H)[f] | |
| | | | | 3.877 (2 H) | |
| | | | | 2.905 (2 H) | |
| | | | | 2.818 (2 H) | |
| | | | | 0.395 (2 H) | |
| | | | | 0.235 (2 H) | |
| 2,8-Dimethylperylene$^{+\bullet}$ | −60 | | | [4.202 (2 H)][f,l] | |
| | | | | [4.069 (2 H)] | |
| | | | | [3.135 (2 H)] | |
| | | | | 2.635 (2 H) | |
| | | | | 0.464 (2 H) | |
| | | | | 0.299 (2 H) | |

**Table** 3 (*continued*)

| Compound[a] | $T$/°C[b] | $g$[c] | Position | Splitting constant (G) This work[d] | Splitting constant (G) Other |
|---|---|---|---|---|---|
| 3*H*,10*H*-acenaphtho[1,2-*c*]-1,2-dithiete$^{+\cdot m}$ | −50 | 2.006 | 1 | 9.5 | |
| | | | 2 | 1.80 | |
| | | | 3 | 1.05 | |
| | | | 4 | 4.60 | |

[a] Where the compound name is shown in parentheses the radical formed is derived from this compound. [b] Error ±5 °C. [c] Error ±0.0002. [d] Error ±0.006 G unless otherwise indicated. [e] Error ±0.001. [f] Assignment uncertain, the number of protons is given in parentheses. [g] From ref. 11. [h] See also ref. 19. [i] From ref. 4. [j] From ref. 10. [k] From ref. 22. [l] Splitting constants in parentheses are tentative only. [m] From the reaction of 1,8-dimethylnaphthalene with $AlCl_3$–$SOCl_2$.



Scheme 1.

*Methylnaphthalene* 1,8-*Disulphide Cation Radicals*.—Naphthalene, 1- and 2-monomethyl-, and 1,2-, 1,3-, 1,6-, 1,7-, 1,8-, 2,3-, 2,6-, and 2,7-dimethyl-naphthalene all react to produce a cation radical which we attribute to derivatives of naphtho[1,8-*cd*]-1,2-dithiole (**1**). We will refer to these products as disulphides. That the cation radicals formed are all part of one series is shown clearly by the $g$ values and the existence of a satisfactory additivity relationship for the three independent sets of splitting constants. The refined additivity parameters and the splitting constants predicted are given in Table 2.

The proportion of naphthalene disulphide formed to perylene formed was highest for 2-methylnaphthalene and 2,7-dimethylnaphthalene, for which very little perylene was observed, and lowest for 1,3-, 1,7-, and 1,8-dimethylnaphthalene for which the naphthalene disulphide spectra observed were all very weak.

Our reasoning for attributing this series to naphtho[1,8-*cd*]-1,2-dithiole is as follows. (a) No more than six splitting constants were required to satisfactorily fit the observed e.s.r. spectra, indicating that the product is a disubstituted naphthalene radical. 1,8-Dimethylnaphthalene gives a product requiring only three splitting constants, indicating that the product must be symmetrically substituted at the 2 and 7, 3 and 6, or 4 and 5 positions. Assuming there is no methyl migration, either during formation of the disulphide or of the cation radical formed therefrom, the product must be substituted at the 4 and 5 positions, as 2,3-, 2,6-, and 2,7-dimethylnaphthalene all give this type of product. The assumption of no methyl migration can be justified on the basis that if methyl migration occurred 1,4- and 1,5-dimethyl- and 1,2,4-trimethyl-napthalene would also be expected to give this type of product.

**Table 4.** Additivity parameters for proton splitting constants of methylnaphthalene radical cations

| Parameter | Experimental | Calculated[a] |
|---|---|---|
| $a_1$[b] | $(-5.40 \pm 0.30^{c})^{d}$ | $-5.39 \pm 0.10$ |
| $\Delta_{12}$ | $-0.47 \pm 0.11$ | $-0.73 \pm 0.08$ |
| $\Delta_{13}$ | $-0.12 \pm 0.13$ | $0.20 \pm 0.08$ |
| $\Delta_{14}$ | $(-0.79)$ | $-0.92 \pm 0.08$ |
| $\Delta_{15}$ | $(0.46)$ | $0.55 \pm 0.07$ |
| $\Delta_{16}$ | $0.59 \pm 0.07$ | $0.86 \pm 0.07$ |
| $\Delta_{17}$ | $-0.33 \pm 0.07$ | $-0.31 \pm 0.07$ |
| $\Delta_{18}$ | $(1.00)$ | $1.05 \pm 0.07$ |
| Overall standard deviation | 0.12 | 0.14 |
| $a_2$ | $-1.82 \pm 0.08$ | $-1.07 \pm 0.06$ |
| $\Delta_{21}$ | $-0.55 \pm 0.05$ | $-0.80 \pm 0.05$ |
| $\Delta_{23}$ | $1.20 \pm 0.08$ | $1.06 \pm 0.05$ |
| $\Delta_{24}$ | $0.22 \pm 0.05$ | $0.42 \pm 0.05$ |
| $\Delta_{25}$ | $0.51 \pm 0.06$ | $0.45 \pm 0.04$ |
| $\Delta_{26}$ | $-0.65 \pm 0.06$ | $-0.80 \pm 0.05$ |
| $\Delta_{27}$ | $0.66 \pm 0.06$ | $0.80 \pm 0.05$ |
| $\Delta_{28}$ | $-0.07 \pm 0.06$ | $-0.23 \pm 0.04$ |
| Overall standard deviation | 0.08 | 0.09 |

[a] Calculated from INDO calculations for the individual radical ions. [b] The contribution to the splitting constant at position $K$ made by a methyl group at position $J$ is $\Delta_{KJ}$, where the molecular symmetry is used to orient the molecule to minimise the value of $K$. [c] The error given is the estimated parameter standard deviation. [d] The values given in parentheses are determined using the value for $a_1$ in powder from ref. 31.

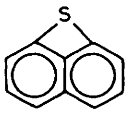
(b) The $g$ value of 2.008 is indicative of an aromatic radical ion containing a heteroatom. Of the possible heteroatoms present in the reaction mixture chlorine and aluminium are unlikely due to the absence of any hyperfine splitting from $^{35}Cl$, $^{37}Cl$, or $^{27}Al$. Sulphur and oxygen remain as possibilities. Contributions due to the odd isotopes, $^{33}S$ or $^{17}O$ in natural abundance, are less than the noise level and therefore undetectable. Most oxygen-containing aromatic radicals or radical cations have $g$ values between 2.002 and 2.003. Given that the e.s.r. spectrum of this product is not observed in the absence of $SO_2$, $SOCl_2$, and $S_2Cl_2$, the incorporation of sulphur is indicated.

(c) The e.s.r. spectrum assigned to the disulphide is very similar to that of genuine samples of naphtho[1,8-*cd*]-1,2-dithiole reported by a number of groups. The various reports of the spectral parameters of naphtho[1,8-*cd*]-1,2-dithiole are summarised in Table 5.

**Table 5.** Splitting constants and $g$ values of naphtho[1,8-*cd*]-1,2-dithiole$^{+\bullet}$

| Splitting constant (G) | $g$ | Ref. |
|---|---|---|
| 5.30, 4.44, 0.88 | 2.0081 | *a* |
| 5.20, 3.85, 0.70 | | *b* |
| 5.52, 4.56, 0.96 | 2.007 | *c* |
| 5.25, 4.32, 0.96 | 2.0086 | 21 |
| 5.26, 4.42, 0.88 | 2.0086 | This work |

[a] A. Zweig and A. K. Hoffman, *J. Org. Chem.*, 1965, **30**, 3997. [b] B. I. Stepanov, W. Ya. Rodinov, A. Ya. Zheltov, and V. V. Orlov, *Tetrahedron Lett.*, 1971, 1079. [c] F. B. Bramwell, R. C. Haddon, F. Wudl, M. L. Kaplan, and J. H. Marshall, *J. Am. Chem. Soc.*, 1978, **100**, 4612.



**(2)**

(d) There are a number of related compounds which might be expected to have similar e.s.r. spectra. These are the radicals from the dioxide and tetraoxide of naphtho[1,8-*cd*]-1,2-dithiole, naphtho[1,8-*bc*]thiete (**2**), and the mono-oxide and dioxide thereof.

The oxides had been eliminated as possibilities on the basis of ionisation potentials.[20] Later work with $SOCl_2$ and $S_2Cl_2$ supported this conclusion, as both $SOCl_2$ and $S_2Cl_2$ gave the same product as $SO_2$.

(e) This leaves only naphtho[1,8-*bc*]thiete as an alternative. The ionisation potential of naphtho[1,8-*bc*]thiete[21] is 8.28 eV, which is higher than the accepted oxidation potential[12] of $AlCl_3$ in $CH_2Cl_2$ of *ca.* 8.0 eV.

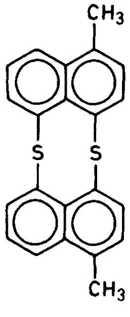
We therefore consider that the compounds formed are the methyl derivatives of naphtho[1,8-*cd*]-1,2-dithiole rather than of naphtho[1,8-*bc*]thiete.

Conclusive proof of the presence of sulphur in the radical cation will be obtained when experiments involving sulphur dioxide enriched with $^{33}S$ ($I\ \frac{1}{2}$) are carried out.

The assignments for the methylnaphthalene disulphide radicals were made using the additivity relationship, which successfully resolved any ambiguities in assignment.

*Methylperylene Cation Radicals.*—In most cases where the disulphide radical ion was observed, a signal with $g$ *ca.* 2.003 was also observed. For naphthalene and 1,7-dimethylnaphthalene, this signal was sufficiently strong for the spectra to be successfully simulated. The spectrum observed from naphthalene we assign to perylene$^{+\bullet}$. The splitting constants observed for this species were in reasonable agreement with those reported for perylene$^{+\bullet}$ by Reymond and Fraenkel[22] for a known sample of perylene. Perylene is also the expected product from the Scholl condensation of naphthalene. The conditions required for the Scholl condensation are similar to those used in the present study.

The signal with $g$ 2.003 from reaction of 1,7-dimethylnaphthalene was successfully simulated with four doublet and two sextet splitting constants, which is consistent with the anticipated spectrum from a tetramethyl-substituted perylene formed by the Scholl condensation. Either 2,4,8,10- or 2,4,9,11-tetramethylperylene is the expected product, and it is impossible to distinguish between the two solely on the basis of the number of splitting constants. The spectra of authentic samples of 2,8- and 3,9-dimethylperylene$^{+\bullet}$ were recorded in an attempt to resolve the above ambiguity. The simulated splitting constants are given in Table 3. If 2,4,8,10-tetramethylperylene was formed, then a simplified additivity relationship could be produced by use of the symmetry of the compound. However since no satisfactory additivity relationship could be found for the various assignments used, 2,4,9,11-tetramethylperylene is thought to be formed, and the data are recorded as such in Table 3.



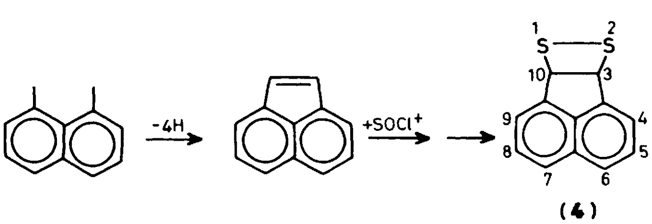
**(3)**

*E.s.r. Signal with* g ca. 2.015.—2-Methyl- and 1,2-, and 1,4-dimethyl-naphthalene each gave signals with $g$ 2.015, 1,4-dimethylnaphthalene on reaction with $SO_2$, the others when $SOCl_2$ was used. Makela *et al.*[23] observed a signal with $g$ 2.0154 from the reaction of 1,2,3,6,7,8-hexahydropyrene with $HFSO_4$. On the basis of earlier work by Gilbert *et al.*[24] this signal was attributed to a sulphinyl radical. However, the sulphinyl radicals reported by Gilbert *et al.* had $g$ values of *ca.* 2.010. We believe that the difference is too large to be explained by any structural effects. It seems possible that the signals observed by us and by Makela *et al.* are produced by multiple sulphinylation. No further identification of the species responsible was possible.

*E.s.r. Signals with* g ca. 2.005.—1,4-Dimethyl- and 1-methylnaphthalene both reacted with $SO_2$ to give products with $g$ *ca.* 2.005. In the signal from 1,4-dimethylnaphthalene, hyperfine splitting was apparent, but the linewidth was too large to allow any meaningful simulation of the spectrum. In the signal from 1-methylnaphthalene the linewidth was sufficiently narrow to enable the spectrum to be successfully simulated. The splitting constants given in Table 3 indicate that the species producing the e.s.r. spectrum, consists of two naphthalene moieties symmetrically bridged by two or more sulphurs. A possible structure is (**3**).

3H,10H-*Acenaphtho*[1,2-c]*dithiete* (**4**).—1,8-Dimethylnaphthalene reacts with $SOCl_2$–$AlCl_3$ to give a spectrum which contains that of a species centred at $g$ 2.006. The splitting constants given in Table 3 satisfactorily simulate the observed spectrum. The $g$ value indicates that it comes from a species containing one or more sulphur atoms. The observation of four pairs of splitting constants indicates that the radical formed must be symmetric. The magnitude of the 9.5 G splitting constant indicates that the above hydrogens must lie substantially out of the plane of the molecule. (*cf.* 13.18 G observed by Buchanan *et al.*[25] for acenaphthene$^{+\bullet}$) However as there are only two hydrogens with this splitting constant, a carbon–carbon bond must exist between C-3 and C-10; C-3, and C-10 must also be bridged by one or more sulphurs. The sulphurs would be expected to lie out of the plane of the molecule. Because of the steric strain caused by the C-3–C-10 bond[26,27] we believe that the disulphide would be considerably more stable than the monosulphide, and hence is more likely to be the observed product.

The other splitting constants were assigned by comparison



**(4)**

**Scheme 2.**

with the splitting constants in the naphthalene disulphide cations and in 1,8-dimethylnaphthalene cation.

In light of the strongly dehydrogenating conditions[13] we postulate the formation of acenaphthylene as an intermediate (Scheme 2). Work by Dubois *et al.*[28] suggests that the electrophile is $SOCl^+$ rather than $SO_2^+$. $AlCl_3$ reacts with $SO_2$ to form $AlOCl_2^-$ and $SOCl^+$. It would therefore be expected that $AlCl_3$ would readily react with $SOCl_2$ to form $SOCl^+$ and $AlCl_4^-$, and that the $SOCl^+$ formed would then add to the double bond in the acenaphthylene which we have postulated as an intermediate.

*Signals with* g 2.003.—Naphthalene, 1,8-, 2,6-, and 2,3-dimethylnaphthalene all give spectra which contained that of a species centred at *g ca.* 2.003. The spectrum observed from naphthalene is in addition to the dimer cation or perylene cation already identified, and some other species such as the binaphthyl$^{+\bullet}$ must be postulated. A similar situation exists for 1,8-dimethylnaphthalene where the observed spectrum is in addition to the previously identified dimer cation radical or the 3,4,9,10-tetramethylperylene$^{+\bullet}$, which would be the expected product from the Scholl condensation of 1,8-dimethylnaphthalene. It seems likely that the species responsible is the radical cation of the binaphthyl Scholl condensation intermediate or of some further condensed form.

2,3- and 2,6-dimethylnaphthalene also gave simple spectra centred at *g* 2.003. Because a dimer would give simpler spectra than a perylene or other condensation product, we have tentatively ascribed the signals observed to the radical cations of the dimers of these two compounds.

*Conclusions.*—The observation of a variety of cation radicals provides only an indication of the complexity of the reactions occurring. There are a number of factors which require consideration in assessing the relevance of the e.s.r. results. These are: (1) the intensity of the observed e.s.r. spectra indicates that the species observed represent no more than 10% of the starting material. (2) E.s.r. spectra, under the conditions of this study, will only be observed from species with an ionisation potential[21] of less than 8 eV. (3) If there is insufficient $AlCl_3$ present to oxidise all the parent compound and any products formed, charge transfer will occur, and e.s.r. spectra will be observed only from the more stable species. The ionisation potential of naphthalene disulphide[21] is 7.14 eV, that of perylene[29] is 7.45 eV, and that of naphthalene[30] 8.12 eV. It would therefore be expected that any disulphide formed would be ionised in preference to any perylene formed, and to the parent methylnaphthalene. Therefore, if any perylene signal is present, all the naphthalene disulphide will have been ionised, and the signal intensity will be directly related to the amount of naphthalene disulphide present.

The reaction of $SO_2$ with 2-methyl- and with 2,7-dimethylnaphthalene to yield products substituted at the 1 position rather than the 4 position indicates that the reaction step which controls formation of the observed products is electrophilic addition. A likely electrophile is $SOCl^+$ which is known[28] to be present under the reaction conditions used.

The additivity relationship for the methylnaphthalene monomer cations is summarised in Table 4. The value of the $\alpha$-splitting constant for crystalline naphthalene found by Owen and Vincow[31] has been used as an estimate of the splitting constant in solution. Included for comparison purposes is an additivity relationship calculated from the splitting constants calculated for the individual ions using the INDO method.[18] The agreement is poor, but does indicate that the experimental values are approximately correct. As the number of observations for each parameter is low (22 observations of 16 parameters) the estimated standard deviation does not provide a very good estimate of the true error in the additivity parameters. Given the paucity of observations, the agreement between the experimental and calculated additivity relationships is considered satisfactory.

## Acknowledgements

This work was supported in part by a grant from the University Grants Committee of New Zealand and one of us (M. G. B.) is grateful for a postgraduate scholarship.

## References

1 C. de Waard and J. C. M. Henning, *Phys. Lett.*, 1963, **4**, 31.
2 F. Gerson, B. Weidmann, and E. Heilbronner, *Helv. Chem. Acta*, 1964, **47**, 1951.
3 R. E. Moss, N. A. Ashford, R. G. Lawler, and G. K. Fraenkel, *J. Chem. Phys.*, 1969, **51**, 1765.
4 F. Gerson, B. M. Peake, and G. M. Whitesides, *Org. Magn. Reson.*, 1972, **4**, 361.
5 C. M. Kirk, Ph.D. Thesis, University of Canterbury, 1975.
6 S. Brumby, *J. Magn. Reson.*, 1980, **40**, 157.
7 M. Bakker, R. F. C. Claridge, and C. M. Kirk, unpublished work.
8 I. C. Lewis and L. S. Singer, *J. Chem. Phys.*, 1965, **43**, 2712.
9 O. W. Howarth and G. K. Fraenkel, *J. Chem. Phys.*, 1969, **52**, 6258.
10 K. D. J. Root and M. T. Rogers, *J. Magn. Reson.*, 1969, **1**, 568.
11 H. Yoshimi and K. Kuwata, *Mol. Phys.*, 1972, **23**, 297.
12 H. Bock and W. Kiam, *Acc. Chem. Res.*, 1982, **15**, 9.
13 M. Bakker, R. F. C. Claridge, and B. M. Peake, unpublished work.
14 B. M. Peake, Ph.D. Thesis, University of Canterbury, 1971.
15 A. T. Balaban and C. D. Nenitzescu, 'Friedel-Crafts and Related Reactions,' Wiley, New York, 1963—1965 vol. II, ch. 23.
16 J. Heinzer, ESRCON, obtained from the Quantum Chemistry Program Exchange, Program Number 197.
17 J. A. Pople, D. L. Beveridge, and P. A. Dobosh, *J. Chem. Phys.*, 1967, **47**, 2026.
18 P. E. Stevenson and D. L. Burkey, *J. Am. Chem. Soc.*, 1974, **96**, 3061.
19 M. Bakker and R. F. C. Claridge, *J. Magn. Reson.*, 1986, **67**, 438.
20 M. Bakker, Ph.D. Thesis, University of Canterbury, 1985.
21 H. Bock, G. Brahler, D. Dauplaise, and J. Meinwald, *Chem. Ber.*, 1981, **114**, 2622.
22 A. Reymond and G. K. Fraenkel, *J. Phys. Chem.*, 1967, **71**, 4570.
23 R. Makela, M. Oksanen, and M. Vuolle, *Acta Chem. Scand., Ser. A.*, 1984, **38**, 73.
24 B. C. Gilbert, C. M. Kirk, R. O. C. Norman, and H. A. H. Laue, *J. Chem. Soc. Perkin Trans. 2*, 1977, 497.
25 A. C. Buchanan III, R. Livingston, A. S. Dworkin, and G. P. Smith, *J. Phys. Chem.*, 1980, **84**, 423.
26 H. W. W. Ehrlich, *Acta Crystallogr.*, 1957, **10**, 699.
27 R. A. Wood, T. R. Welberry, and A. D. Rae, *J. Chem. Soc., Perkin Trans. 2*, 1985, 451.
28 J. E. Dubois, M. Delmar, and P. C. Lacaze, *Electrochim. Acta*, 1980, **25**, 429.
29 M. J. S. Dewar and D. W. Goodman, *J. Chem. Soc., Faraday Trans. 2*, 1972, **68**, 1794.
30 V. I. Vedeneev, L. V. Gurvich, V. N. Kondrat'yev, V. A. Madvedev, and Y. L. Frankevich, 'Bond Energies, Ionization Potentials and Electron Affinities,' Edward Arnold, London, 1966.
31 G. S. Owen and G. Vincow, *J. Chem. Phys.*, 1971, **54**, 368.

*Received* 13*th January* 1986; *Paper* 6/099