ESR studies of free radicals derived from hydroxyquinones

I. Group 14 adducts of hydroxynaphthoquinones

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Abstract

The group 14 organometallic radical adducts of 1,4-naphthoquinone, lawsone, juglone, plumbagin, and naphthazarin have been investigated by ESR spectroscopy. The results are discussed in terms of the regioselectivity of the addition reaction, the effects of hydroxyl substituent and intramolecular hydrogen bonding on the electron spin density distribution, and the effects of varying the group 14 metal from silicon to lead.

Introduction

Hydroxy-naphthoquinones and anthraquinones are widespread in nature and have important applications, for example, as dyestuffs and pharmaceuticals [1]. The semiquinone radical anions of these compounds have been extensively investigated by ESR [2], indeed it has been suggested that this form of spectroscopy provides a useful analytical technique for assigning the pattern of substitution in these compounds [3,4]. Neutral radicals derived from these substrates have, however, received rather less attention.

The semiquinone radicals derived from 1,4-naphthoquinone (NQ) and 9,10-anthraquinone (AQ) have been generated by photolysis of the quinones in hydrogen atom donating solvents such as dioxane [5]. This well-known photochemical reaction has been extensively employed in studies on benzoquinones. The resulting semiquinones can be regarded as hydroxy-substituted phenoxyl, 1-naphthoxyl, or 9-anthracenoxyl radicals. The general features of the unpaired electron distribution in naphthalene derived radicals of this type has been elucidated by Dixon and his
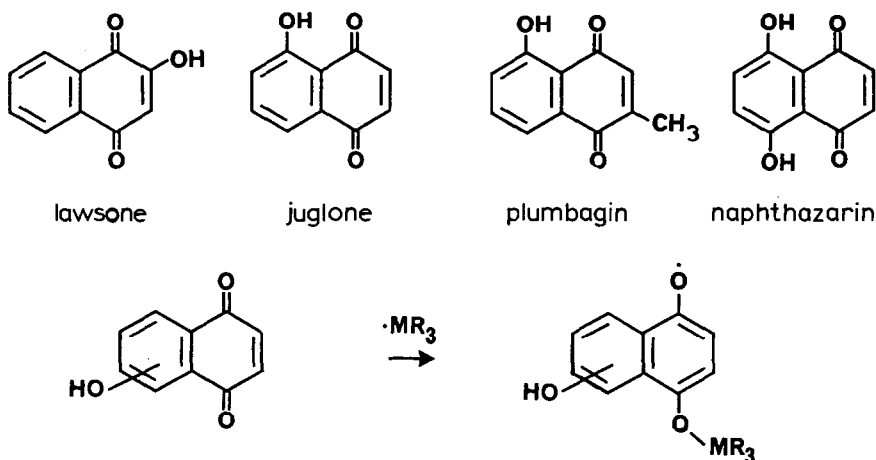
Scheme 1

coworkers, who oxidised substituted naphthols with cerium(IV) ions in a flow system [6]. However, the spectra derived from dihydroxynaphthalenes were complicated by the effects of rapid proton exchange with the aqueous acidic medium employed in the experiments. Recently information has been obtained on the 1-naphthylmethyl radical which may be regarded as the prototype for this type of system [7].

Radicals closely related to neutral semiquinones are formed by the addition of silyl and other group 14 metal-centred radicals to the carbonyl groups of quinones [8], a reaction which has been the subject of numerous ESR studies [9]. The addition of silyl, germyl and stannyl radicals to NQ and AQ was reported in 1978 [10]. The present paper deals with an extension, of this work to include four hydroxy-substituted naphthoquinones: lawsone (2-hydroxy-NQ), juglone (5-hydroxy-NQ), plumbagin (2-methyl-5-hydroxy-NQ) and naphthazarin. We have also completed the series by preparing the corresponding adducts with lead radicals.

The overall reaction sequence is as shown in Scheme 1, where M is Si, Ge, Sn or Pb. The actual mechanism may be more complicated. Recent work on the addition of silyl radicals to substituted benzoquinones has shown that at low temperatures preferential addition occurs to a ring carbon atom. This kinetically favoured adduct then converts to the thermodynamically favoured oxygen adduct [11]. In our experiments we have observed silyl adducts at high temperatures and have detected addition only to the carbonyl group.

In an unsymmetrically substituted quinone such as lawsone, juglone or plumbagin, there are two possible sites for radical addition and one might expect to see either or both of two isomeric intermediates. The regioselectivity of the addition reaction of group 14 radicals to p-diones has been the subject of previous investigations [12,13]. In general the least-hindered isomer is formed, but there is some suggestion that the presence of an electron-rich atom adjacent to the carbonyl group might stabilise the more hindered isomer by coordinating with the metal atom of the attacking radical [14]. Both possible isomers have been detected in the addition of stannyl and plumbyl radicals to 2,6-dimethoxybenzoquinone [13]. The presence of

an adjacent hydroxyl group in a naphthoquinone might also influence the direction of addition.

A further point of interest lies in the possible influence of intramolecular hydrogen bonding. This may involve either an *ortho* hydroxyl group as in lawsone, or a peri-interaction as in juglone or napthazarin. The special nature of an H-bonded proton bridging the 1,8-positions in naphthalene has been discussed in many studies involving the radical ions of naphthazarin and its derivatives [4,15–18].

Experimental

The quinones used in this work were all obtained commercially, as were the radical precursors triphenylsilane, triphenylgermane, hexabutyldistannane, tributylstannane, and hexaphenyldiplumbane. The radicals were obtained using well established procedures [10]. For silyl and germyl adducts the best ESR spectra were generally obtained by melting the quinone and triphenylsilane or triphenylgermane, either as a binary mixture or dissolved in biphenyl. The tin and lead radicals were prepared by photolysis of solutions of the quinone, the ditin or dilead compound, and di-t-butyl peroxide in THF or t-butylbenzene. The ESR spectra was recorded on Varian E104 or Bruker ER200 spectrometers. A 1 kW high pressure mercury lamp was used as a source of UV light. Some typical spectra are shown in Fig. 1 and the hyperfine coupling constants, obtained by computer simulation, are summarised
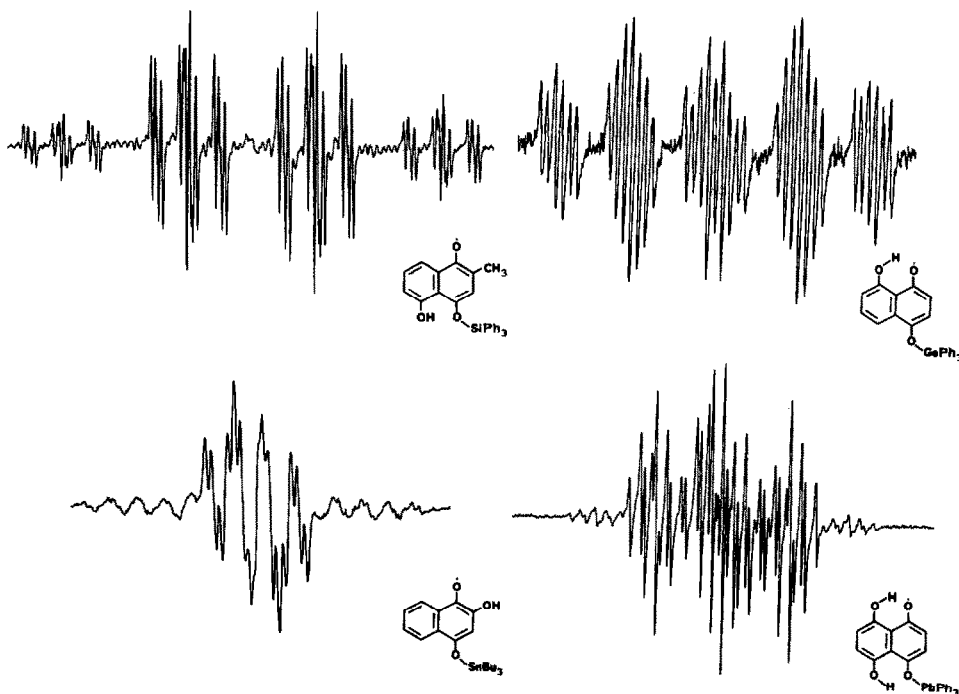

Fig. 1. ESR spectra observed during the reactions of triphenylsilyl radicals with plumbagin, triphenylgermyl radicals with juglone, tri-n-butylstannyl radicals with lawsone ($a(^{119}Sn) = 10.6$ G), and triphenylplumbyl radicals with naphthazarin ($a(^{207}Pb) = 7.5$ G).

0.64 O·

2.14

0.64

2.14 O–SiPh₃

8.45

1.52

0.51 O·

1.98

0.54

1.86 O–GePh₃

8.05

1.16

0.4 O·

1.85

0.52

1.85 O–H

7.67

0.8

0.25 O·

1.58

0.25

1.3 O–SnBu₃

6.59

0.25

0.15 O·

1.40

0.15

1.25 O–PbPh₃

6.15

0.55

0.16 O·

0.97

0.29

0.72 O⁻Li⁺

4.62

1.92

0.13 O·

0.81

0.36

0.49 O⁻Na⁺

4.15

2.41

0.14 O·

0.85

0.44

0.46 O⁻K⁺

3.87

2.62

0.16 O·

0.82

0.41

0.43 O⁻Cs⁺

3.82

2.70

0.31 O·

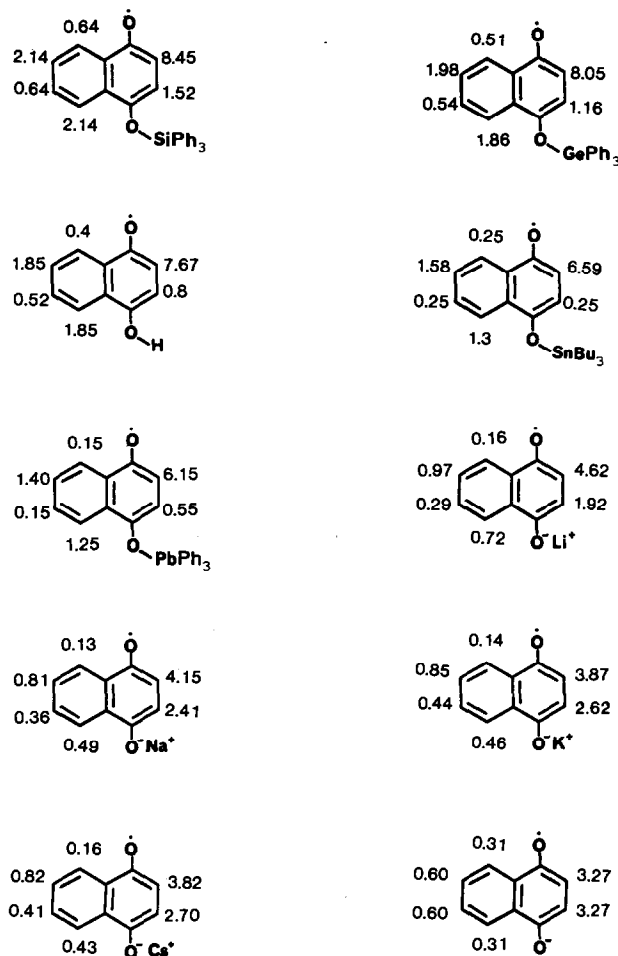0.60

0.60

0.31 O⁻

3.27

3.27

Fig. 2. The hyperfine coupling constants (G) of some radical adducts and radical ion-pairs of 1,4-NQ. Data from references 5, 10, 20 and this work.

in Figs. 2 and 4. In the case of the tin and lead adducts it was generally possible to observe metal satellite splittings. These couplings (cf. Fig. 1) were in the range normally observed for this type of radical [10,19].

Results and discussion

The effect of the metal

The variation in hyperfine coupling constants observed on descending the Periodic Table from Si to Pb is best illustrated by considering the adducts formed by NQ. The results are summarised in Fig. 2 where we have also included some recently published data [20] on radical-ion-pairs formed by alkali-metal reduction of NQ. The data nicely illustrate the effect on the spin distribution of increasing ionic character of the metal–oxygen bond.
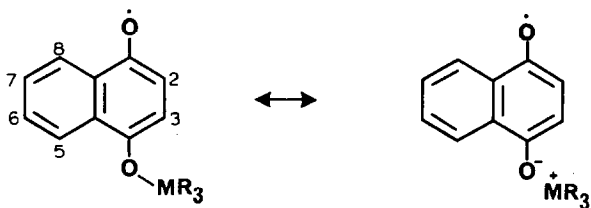
Consider the values of $a(2)$ and $a(3)$ which would be equal in the unperturbed radical anion. If the sign of $a(3)$ changes from positive to negative between the germyl and stannyl adducts, the magnitude of the sum of $a(2)$ and $a(3)$ (6.93, 6.89, 6.84, 6.7 G) shows only a small decrease on going to the heavier elements. For the alkali-metal ion-pairs the sum of $a(2)$ and $a(3)$ is ca. 6.55 G with a decreasing perturbation on going from Li to Cs. These observations are not entirely unexpected. It was recognised many years ago that the algebraic sum of the *ortho* and *meta* coupling constants in a *para*-substituted phenoxyl radical is approximately independent of the substituent [21,22].

In an attempt to support our assignment of the coupling constants, we have performed molecular orbital calculations on a model system. Trial calculations used INDO and related methods gave disappointing results. The failure of the INDO method [23] to give good spin densities for phenoxyl radicals has been noted by previous investigators [22,24]. We have, therefore, resorted to McLachlan's semi-empirical SCF method [25] which is known to work well for this type of system.

A wide range of parameters have been employed in the application of this method to semiquinone and phenoxyl radicals. Gough [26] obtained an excellent fit for the benzosemiquinone radical but his parameters seem to work less well for naphthoquinones. Murphy [24] has shown that improved results for naphthoxyl radicals can be obtained by varying the resonance integrals for C–C bonds to allow for deviations from regular hexagonal rings but the resulting values seem rather
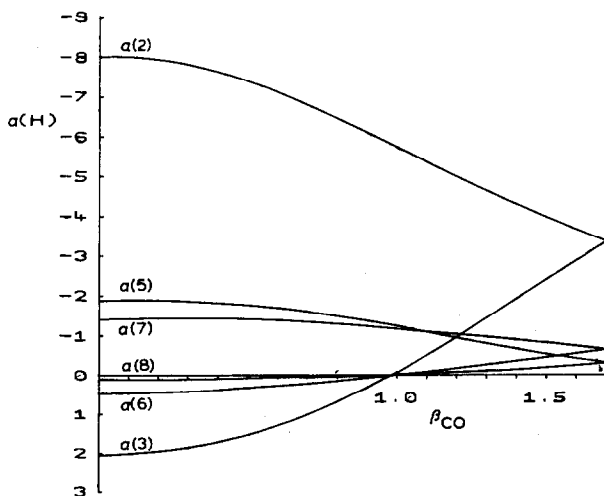

Fig. 3. Calculated proton coupling constants for adducts of 1,4-NQ as a function of the resonance integral for the C–O bond to which addition has occurred.
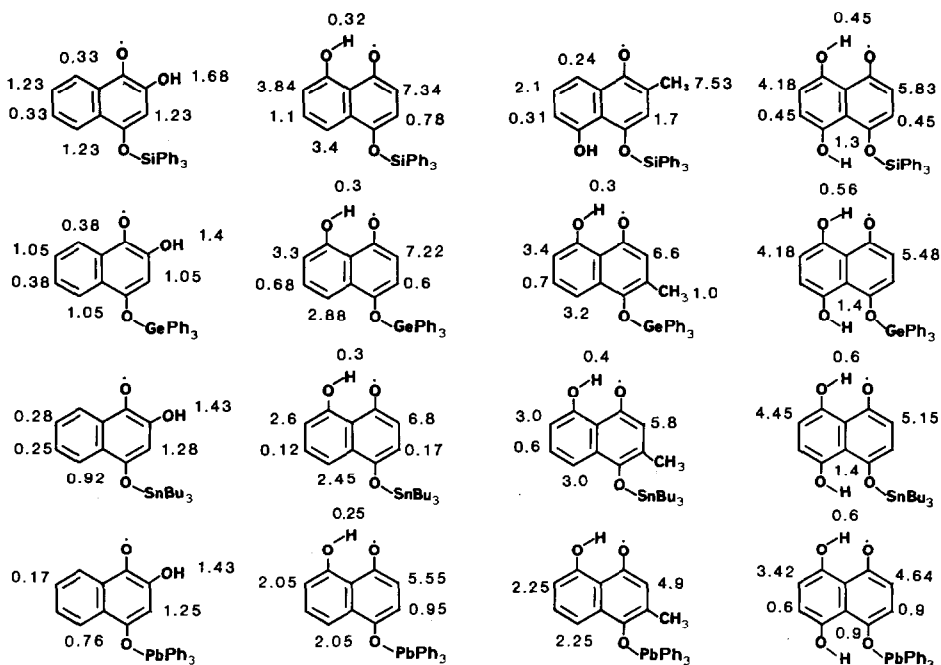
Fig. 4. The proton splittings (G) for group 14 adducts of lawsone, juglone, plumbagin, and naphthazarin.

extreme. We have, therefore, based our calculations on the work of Flint and Tabner [20] who obtained a good fit to the spin density distribution in the unperturbed NQ radical anion with $\alpha_O = \alpha + 1.4\beta$, $\beta_{CO} = 1.7\beta$, $Q = -22$ G, and $\lambda = 1.2$. We have simulated the perturbation on the second oxygen atom by allowing the resonance integral for the C–O bond to vary between 0 and 1.7β. In the lower limit the calculation corresponds to an unsubstituted 1-naphthoxyl radical and in the upper limit to the free NQ radical anion. The results are plotted in Fig. 3. They reproduce the observed tends well and lend support to our assignment of the coupling constants.

The same arguments can be applied to the hyperfine coupling constants for the adducts formed by hydroxy-substituted naphthoquinones (Fig. 4) which show similar trends as the metal is varied.

Regioselectivity

When an organometallic radical adds to an unsymmetrically substituted quinone such as lawsone there are two possible sites for radical addition leading to structures A and B.

(A)   (B)
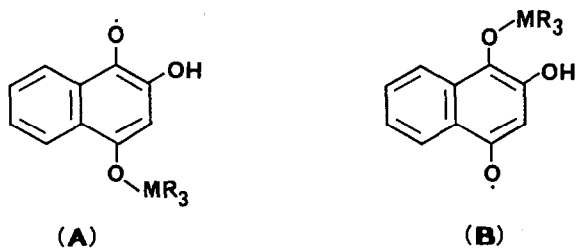
The 4-adduct (A) is less hindered but the 1-adduct (B) might be stabilised by coordination of the metal atom, particularly tin or lead, to the hydroxyl group. The alternatives are easily distinguished by their ESR spectra. In practice all the adducts obtained from lawsone gave narrow spectra lacking the large doublet splitting expected for B and have been assigned to structure A. The spectrum of the tributylstannyl adduct is shown in Fig. 1. Similarly, juglone also invariably gave rise to the less hindered adduct (e.g. the triphenylgermyl adduct shown in Fig. 1) with no detectable ESR signals attributable to the other isomer. The most interesting behaviour is shown by plumbagin. The predominant ESR spectrum obtained on reaction with triphenylsilyl radicals exhibits a large quartet splitting (Fig. 1), indicating that addition has occurred at the 1-position, whereas the other group 14 radicals gave narrower spectra consistent with addition adjacent to the methyl group.

These results suggest that an hydroxyl group adjacent to the site of addition does not have a stabilising influence and that the selectivity of the addition is mainly influenced by steric factors. However, the relative stabilities of the two isomeric products may also be important since the position of a hydroxyl substituent relative to the phenoxyl group can have a significant effect on the spin density distribution. In general the most stabilised product is obtained. The anomalous behaviour of plumbagin towards triphenylsilyl radicals may be a consequence of steric hindrance by the methyl group preventing formation of the most stabilised adduct. This may be less significant in the case of the other group 14 elements because of the increased length of the metal–oxygen bond.

Substituent effects

We have already commented on the trends in coupling constants apparent in the vertical columns of Fig. 4. There are also horizontal variations attributable to the hydroxyl substituents. It is clear that an hydroxyl group increases the spin density in the ring which has been substituted and that there is much more delocalisation in the adducts of juglone and naphthazarin.

The hydroxyl group in lawsone actually has a rather small effect on the coupling constants and the radicals are essentially substituted 1-naphthoxyls. However, when the hydroxyl group is in a peri-position there is a strong interaction involving a hydrogen bond across the 1,8-positions. This type of situation is well known in the radical ions of naphthazarin and its derivatives [3,15–18]. INDO calculations [18] suggest a linear and symmetrical OHO configuration. However, a rapid exchange involving a double minimum potential is also a possibility. McLachlan spin density calculations give a reasonable account of the spin density distribution observed in the radicals derived from juglone if the oxygen atoms in positions 1 and 8 are treated as equivalent. Similar considerations apply to the radical adducts of naphthazarin.

Dynamic effects

The ion-pairs formed by the radical anion of NQ with alkali metal cations exhibit linewidth alternation in their ESR spectra [20]. This has been attributed to intramolecular cation migration and in principle similar effects might be observed for the group 14 adducts. The migration of silyl, germyl, stannyl, and plumbyl groups has been reported in several adducts formed in 1,2-diones [10,19,27]. However no such

effects have been found in 1,4-diones. This is consistent with the absence of detectable linewidth alternation for the lithium ion pair of NQ. The data in Fig. 1 imply that substantially higher barriers would be expected for the group 14 adducts with their more covalent metal–oxygen bonds.

We have, however, observed some temperature dependence in adducts formed by naphthazarin. For example the triphenylgermyl adduct exhibits doublet splittings of 5.48 and 4.18 G, assigned to positions 2 and 7, at 373 K. At 483 K these doublets are averaged to give a 4.85 G triplet. This process, which appears to be associated with restricted rotation of the hydroxyl group, is also exhibited by the hydrogen atom adduct of naphthazarin and will form the basis of a later publication.

References

1 R.H. Thomson, Naturally Occurring Quinones, Academic Press, London/New York, 1971.
2 J.A. Pedersen, CRC Handbook of EPR Spectra from Quinones and Quinols, CRC Press Inc., Florida 1985.
3 L.H. Piette, M. Okamura, G.P. Rabold, R.T. Ogata, R.E. Moore, and P.J. Scheuer, J. Phys. Chem., 71 (1967) 29.
4 J.A. Pedersen and R.H. Thomson, J. Magn. Res., 43 (1981) 373.
5 S.K. Wong, W. Sytnyk, and J.K.S. Wan, Can. J. Chem., 50 (1972) 3052.
6 W.T. Dixon, W.E.J. Foster, and D. Murphy, J. Chem. Soc., Perkin Trans. 2, (1973) 2124; ibid., (1978) 779.
7 C.J. Rhodes, D. Phil. Thesis. University of Sussex, 1985. C.J. Rhodes and R.A. Jackson, to be published.
8 J. Cooper, A. Hudson and R.A. Jackson, J. Chem. Soc., Perkin Trans. 2, (1973) 1933.
9 K.A.M. Creber, K.S. Chen, and J.K.S. Wan, Rev. Chem. Intermed., 5 (1984) 37.
10 A. Hudson and A. Alberti, J. Chem. Soc., Perkin Trans., 2 (1978) 1098.
11 A. Alberti, C. Chatgilialoglu, G.F. Pedulli, and P. Zanirato, J. Amer. Chem. Soc., 108 (1986) 4993.
12 A. Alberti, A. Hudson, G.F. Pedulli, and P. Zanirato, J. Organomet. Chem., 198 (1980) 145.
13 A. Alberti and G.F. Pedulli, J. Organomet. Chem., 248 (1983) 261.
14 K.S. Chen, T. Foster and J.K.S. Wan, J. Phys. Chem., 84 (1980) 2473.
15 J.R. Bolton, A. Carrington, and P.F. Todd, Mol. Phys., 6 (1963) 169.
16 J.H. Freed and G.K. Fraenkel, J. Chem. Phys., 38 (1963) 2040.
17 J. Gendell, W.R. Miller, and G.K. Fraenkel, J. Amer. Chem. Soc., 91 (1969) 4369.
18 C. Sieiro, A. Sanchez, P. Crouigneau, and C. Lamy, J. Chem. Soc., Perkin Trans. 2, (1982) 1069.
19 A. Hudson, R.A. Jackson, and N.P.C. Simmons, J. Chem. Soc., Perkin Trans. 2, (1977) 1635; A. Alberti, A. Hudson, and G.F. Pedulli, J. Chem. Soc., Faraday Trans., 2, 76 (1980) 948; P.J. Barker, A.G. Davies, J.A.-A. Hawari, and M.-W. Tse, J. Chem. Soc., Perkin Trans. 2, (1980) 1488; A.G. Davies, J.A.-A. Hawari, C. Gaffney, and P.G. Harrison, ibid., (1982) 631.
20 N.J. Flint and B.J. Tabner, J. Chem. Soc., Faraday Trans. 1, 83 (1987) 167.
21 T.J. Stone and W.A. Waters, J. Chem. Soc., (1964) 213.
22 W.T. Dixon, M. Moghimi, and D. Murphy, J. Chem. Soc., Faraday Trans. 2, 70 (1974) 1713.
23 J.A. Pople and D.L. Beveridge, Approximate Molecular Orbital Theory, McGraw-Hill, New York, 1970.
24 D. Murphy, J. Chem. Res. (S), (1980) 321.
25 A.D. McLachlan, Mol. Phys., 3 (1960) 233.
26 T.E. Gough, Can. J. Chem., 47 (1969) 331.
27 A. Alberti and A. Hudson, Chem. Phys. Lett., 48 (1977) 331.