The Radical-cation of *p*-Benzoquinone

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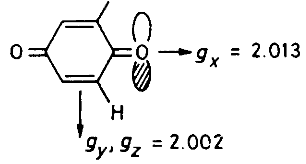
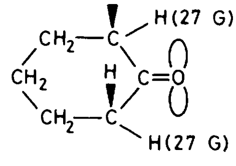
The e.s.r. spectrum assigned to *p*-benzoquinone radical-cations is dominated by a triplet (*ca.* 18.6 G) due to hyperfine coupling to two equivalent protons; this establishes that the SOMO is largely confined to a single in-plane, non-bonding 2p-orbital on oxygen.

It is now well established that radical-cations are formed when dilute solutions of substrate in solvents such as $FCCl_3$ (Freon) are exposed to ionizing radiation at 77 K. A range of organic cations prepared in this way have now been characterised by e.s.r. spectroscopy, including various alkane cations,[1-3] alkene cations,[4] ether cations,[5] and cations of aldehydes and ketones.[6]

In most cases, the SOMO, as revealed by the e.s.r. data, is that expected from the results of photoelectron spectroscopy and theory, one possible exception being the radical cation of pyridine, where the SOMO is clearly the in-plane orbital largely confined to nitrogen rather than the ring π-orbital.[7] The cation of *p*-benzoquinone, not previously studied by e.s.r. spectroscopy, is of interest since the non-bonding, in-plane orbitals are close in energy to the uppermost π-orbital. Also, if the former is the preferred SOMO, does the cation remain symmetrical, or does it distort so that the unpaired electron is confined largely to one oxygen atom?



(1)



(2)

Our results show clearly that the latter possibility is correct [structure (1)]. The e.s.r. spectrum (Figure 1) is characterised by a triplet clearly due to hyperfine coupling to two strongly coupled protons. The central, M_I = 0, feature is asymmetric, indicating considerable g-value anisotropy. The magnetic parameters derived according to the stick diagram in Figure 1 are indicated in (**1**). It is possible that the small (4 G) splitting detected in the low-field line arises through coupling to the remote protons, rather than to g- and A-anisotropy, but we find that spectral simulation is far less satisfactory on this hypothesis (g_x is assigned to the symmetry axis on the expectation that this should give rise to the maximum g-value).

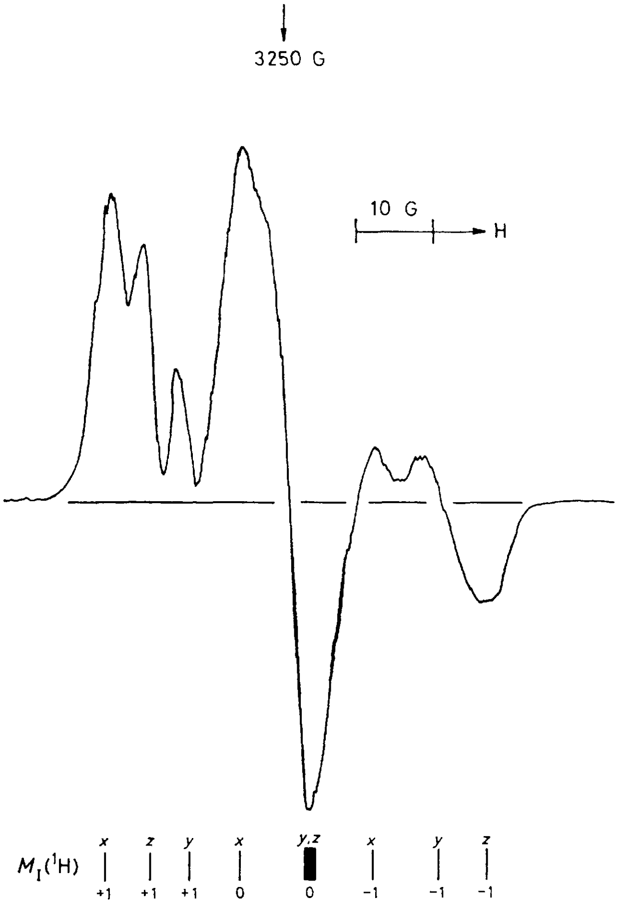


Figure 1. First derivative X-band e.s.r. spectrum for a dilute solution of p-benzoquinone in Freon after exposure to ^{60}Co γ-rays at 77 K, showing features assigned to the radical cation of the quinone. 1 G = 10^{-4} T.

These results are of interest in relation to theoretical[8] and experimental[9] studies on the first excited states of this quinone. According to M.O. theory, the electron is excited from the symmetric or antisymmetric combinations of the oxygen in-plane 2p-orbitals into the π^*-orbital. Simple splitting into the $A_u(n_- \rightarrow \pi^*)$ and $B_{1g}(n_+ \rightarrow \pi^*)$ transitions is not borne out in practice, and it seems that the results are better described in terms of excitations largely confined to one carbonyl group or the other.[9] Our results support this description, and show that the incipient Jahn–Teller distortion indicated by spectroscopic studies is clearly exhibited by the cations, the SOMO being completely confined to one or other carbonyl group. Clearly, the large g-shift is to be associated with field along the O—O axis (x) since this couples the SOMO with the π-orbital. Similar large shifts were observed for simple aliphatic carbonyl radical-cations.[6] Our results for these cations showed that a large proton coupling from 'β' protons only occurred when these are held close to the plane containing the p-orbital axis, as is the case, for example, for the cyclohexanone cation (**2**). It is interesting that this proton coupling is so similar for structures (**1**) and (**2**).

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