Photoisomerisation of Cyclo-octatetraene Radical Cations in a Solid Freon Matrix

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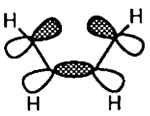
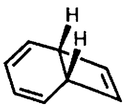
Following γ-irradiation of cyclo-octatetraene in Freon solvents at 77 K, a single central feature was observed by ESR spectroscopy, from the parent radical cation; after bleaching with visible light, this changed to a triplet (36.4 G) of quintets (7.8 G) pattern, assigned to the rearranged cation (**IV**).

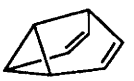
The radical cation of cyclo-octatetraene has been observed in the liquid phase by ESR spectroscopy,[1] and the small coupling (1.5 G) (1 G = 10^{-4} T) observed to eight equivalent protons was interpreted in terms of a non-planar ring, wherein the protons are spin coupled *via* both the mechanisms of spin polarisation and hyperconjugation which partly cancel each other because they deliver negative and positive spin densities, respectively. MINDO/2 calculations support a non-planar structure, although some 'flattening' of the ring from the geometry of the neutral parent molecule is predicted.[2]

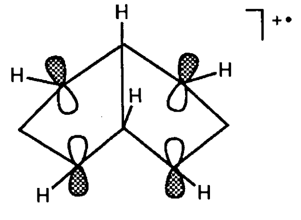
In view of our recent proposal that a rigid Freon matrix can prevent a radical cation rearrangement that is associated with a large change in geometry,[3] we were interested to discover whether a solid matrix could effect any constraints on the geometry of the cyclo-octatetraene radical cation, such that a SOMO was adopted that is similar to the $5a_1$ HOMO of the parent molecule (**I**).[4] If so, it might be expected that the ESR spectrum would show large (positive) couplings to four of the protons, and rather smaller (negative) couplings to the remaining four.

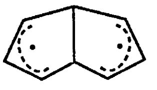
After γ-irradiation of a 0.2% solution of cyclo-octatetraene in $CFCl_3$ to a dose of 1 Mrad at 77 K, the spectrum in Figure 1(a) was recorded. This shows an intense but structureless central line, flanked by weaker features. There seems little doubt that the central line is due to the cyclo-octatetraene radical cation, and the absence of resolved splitting suggests couplings of < *ca.* 3 G (*i.e.* less than the solid state linewidth), which is compatible with the liquid phase value (1.5 G) and so we infer that the solid matrix exerts little influence on the cation geometry. By increasing the gain, the 'wing' features were revealed clearly and can be analysed as the $| \pm 1>$ components of a (2H) triplet (36.4 G) of quintets (7.8 G). Since GC-MS shows the sample of cyclo-octatetraene to be pure (>99%), this additional set of features (clearly not related to the central line, given the disparity in intensities) must be derived from cyclo-octatetraene radical cations. (The absence of any concentration dependence of the relative intensities of the central and wing features argues against the species responsible for the latter being formed through an ion–molecule reaction, and suggests an intramolecular rearrangement.)


(**I**)$5a_1$


(**II**)


(**III**)


(**IV**)


(**V**)

In order to try to promote this rearrangement, we annealed the sample to *ca.* 150 K, but found no increase in the wing signals at the expense of the central line: although an overall loss in intensity occurred, the relative intensities of the two

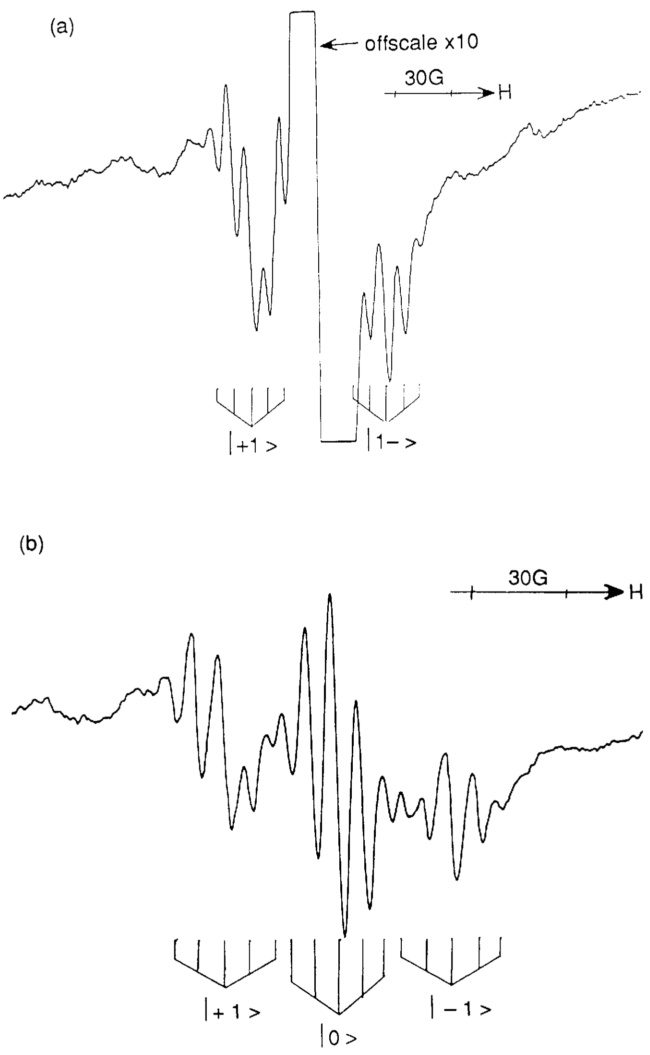


Figure 1. ESR spectra recorded (a) following γ-irradiation of a frozen solution of cyclo-octatetraene in $CFCl_3$ at 77 K, assigned to the parent radical cations (central singlet) and to the rearranged radical cations (**IV**); and (b) following bleaching of the sample in (a) with visible light, and assigned to the radical cations (**IV**).

sets of signals were essentially unchanged. In marked contrast, however, we found that following irradiation of the sample with visible light, the wing features had gained considerable intensity and the central signal from cyclo-octatetraene radical cations had disappeared, so that the $| 0>$ component of the 36.4 G triplet was clearly disclosed, Figure 1(b). It is certain, therefore, that the proposed rearrangement is a photochemical reaction. (Similar results were obtained using a $CF_2ClCFCl_2$ matrix.) To account for the small yield of the rearranged radical observed prior to photo-bleaching, we suggest a degree of 'inadvertent' photolysis; it is probably significant that the sample vials often show a deep blue fluorescence, immediately following γ-irradiation, which may account for this.

As an aid to an assignment of the rearranged cyclo-octatetraene radical cation, we considered the photochemical behaviour of the neutral compound. There are two rearranged products **(II)** and **(III)** that have been reported from the photolysis of cyclo-octatetraene,[5,6] and while the ESR spectrum (b) cannot be easily reconciled with a cation derived from the former structure, it may be readily interpreted as arising from the formation of the radical cation **(IV)** which is analogous to the biradical **(V)**, proposed as an intermediate in the formation of **(III)**.

In **(IV)**, the unpaired electron will be equally distributed between the two allylic units in the b_2 (π-) SOMO which is qualitatively depicted. Therefore, the 7.8 G coupling, at roughly half that measured for the *exo* protons in allyl itself,[7] is assigned to the four equivalent 'allylic' protons and the 36.4 G coupling to the bridgehead protons, which are favourably aligned to interact with the SOMO. Using the Heller–McConnell formula[8] ($A = B\cos^2 \theta$, with a B value of 38 G from our results for the $^2B_2$ state of the hexamethyl Dewar benzene radical cation[3]) a coupling of 38 G is predicted for perfect alignment ($\theta = 0°$), and is close to that observed, although a further enhancement might be expected because this is a 'Whiffen' type system,[9] where hyperconjugation should be reinforced between two interacting sites of appreciable spin density. We note that changes were observed previously in the electronic absorption spectrum[10] of the cyclo-octatetraene radical cation after bleaching with visible light, and it was suggested that a rearrangement of the primary species had taken place, although no firm assignment could be made. The present work proves that this is so, and clearly establishes the identity of the rearranged species.

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