

# Radical cations from dipyridinium derivatives: A combined EPR and DFT study

Pierluigi Stipa\*

*Dipartimento di Scienze dei Materiali e della Terra, Università Politecnica delle Marche, via Brecce Bianche, 60131 Ancona, Italy*

Received 2 May 2005; received in revised form 19 July 2005; accepted 1 August 2005

## Abstract

The monoelectronic reduction of 1,1'-dimethyl-2,2'-dicyano-4,4'-bipyridinium (DCMV<sup>++</sup>) bis-methylsulphate, conducted directly in the cavity of the electron paramagnetic resonance (EPR) spectrometer at room temperature and in DMSO solution, gave the signal of the corresponding radical cation (DCMV<sup>•+</sup>) whose interpretation has been carried out with the aid of density functional theory (DFT) calculations run at different levels. The model chemistries considered yielded in general hyperfine coupling constants (hfcc) in good agreement with the experimental ones, except for the methyl protons directly bonded to the pyridinium nitrogens. The use of various computational methods accounting for solvent–solute interactions did not give significant improvements with respect to the gas phase results, while the geometry optimizations performed showed that the two pyridinium rings are coplanar in the radical cation but staggered in the parent dication, although the corresponding energy barrier involved is very low.

© 2005 Elsevier B.V. All rights reserved.

*Keywords:* EPR; DFT; Radical cations; Viologens

## 1. Introduction

Many of the best-known chemically reversible redox couples contain the quaternized pyridinium system. Notable examples include the NAD<sup>+</sup>/NADH system that functions as an electron-transfer catalyst in the respiratory chain [1], and the various viologens (*N,N'*-di-quaternized 4,4'-bipyridinium salts), which have been employed as herbicides [2], redox mediators [3], electrochromic materials [4,5], electron-transfer quenchers [6], and as redox probes in self-assembled monolayers [7], dendrimers [8], silicates [9], zeolites [10], and semiconductors [11]. This wide range of applicability arise from their easy one-electron reduction which leads to the formation of the corresponding radical cations; some of them show interesting chemical behaviour and physico-chemical properties such as colour development (for this reason are called viologens) and are persistent enough to generate an highly reversible dication/radical–cation redox couple: in order to modulate their potential, which determines the application field, modifications of the main structure have been carried out, varying for example, the group(s) at

the quaternized nitrogen(s) and/or introducing substituents in the pyridine ring(s). With this aim 1,1'-dimethyl-2,2'-dicyano-4,4'-bipyridinium (DCMV<sup>++</sup>), a high redox potential viologen derivative ( $E^\circ = 0.09$  V) [12], has been prepared as bis-methylsulphate salt: during its electrochemical reduction an intense electron paramagnetic resonance (EPR) signal has been recorded but, to our actual knowledge, never described [13].

Electron paramagnetic resonance, in fact, still represents the simplest and probably the most useful experimental technique to directly detect and characterize free radicals, if persistent enough to allows the acquisition of their corresponding spectrum in the spectrometer timescale; unfortunately, the correct interpretation of some of these signals is not straightforward if a large number of splittings is present: in such cases quantum chemical calculations represent a very useful tool to understand the correlation between the radical structure and the hyperfine coupling constants (hfcc) obtained from the spectrum analysis.

In fact, the recent improvements in density functional theory (DFT) [14] yielded computational methods able to describe the properties of free radicals, including their EPR features [15], in satisfactory agreement with experiment; the resulting hfcc values often represent good starting points for the fitting, by

\* Tel.: +39 0712204409; fax: +39 0712204409.  
E-mail address: [p.stipa@univpm.it](mailto:p.stipa@univpm.it).

means of appropriate spectral simulation programs easily available from the EPR community [16], with the corresponding experimental spectra.

In the present paper, we report the results of our study carried out to by means of DFT calculations to obtain a correct interpretation of the EPR spectrum, obtained from the mono-electronic reduction of DCMV<sup>++</sup> in liquid solution, assigned to the corresponding radical cation (DCMV<sup>•+</sup>).

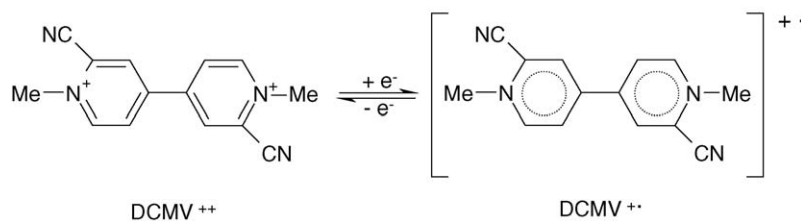
## 2. Experimental

1,1'-Dimethyl-2,2'-dicyano-4,4'-bipyridinium bis-methylsulphate has been prepared as described in the literature [12]. Isotropic X-band EPR spectra have been recorded on a Bruker EMX spectrometer system, equipped with a microwave frequency counter and an NMR gauss meter for field calibration; for *g*-factor determination the whole system has been standardized with a sample of perylene radical cation in concentrated sulfuric acid (*g* = 2.00258); in a typical run, a 10<sup>-4</sup> M argon saturated DMSO solution of DCMV<sup>++</sup> bis-methylsulphate has been added with traces of solid *t*-BuOK (Aldrich) directly in the spectrometer cavity; EPR signals have been acquired using the following spectral parameters: modulation frequency 100 kHz, modulation amplitude 0.2 G, receiver gain 2.24 × 10<sup>4</sup>, microwave power 5 mW, sweep width 50 G, conversion time 1310 ms, and time constant 1.28 ms. EPR spectra simulations have been carried out by means of the Winsim program, freely available from NIEHS [17].

DFT calculations have been performed by means of the Gaussian 03 package [18], mainly on an IBM SP4 supercomputer, with the unrestricted formalism for radical species, yielding  $\langle S^2 \rangle = 0.7500 \pm 0.0003$  for spin contamination (after annihilation); in addition, to confirm that the computed geometries at stationary points were referred to a minimum, frequency calculations were performed in order to verify the presence of imaginary values (negative signs). Isotropic *g*-factor has been determined by means of the gauge independent atomic orbital method [19] as the average of the *xx*, *yy* and *zz* corresponding components.

## 3. Results and discussion

Scheme 1 illustrates the mono-electronic reduction of DCMV<sup>++</sup>; in Fig. 1 the *ball and stick* PBE0/6-31G(d) optimized geometry of the DCMV<sup>•+</sup> radical cation is reported with the arbitrary atom labelling, while the corresponding EPR spectrum, together with its simulation, is shown in Figs. 2 and 3. The interpretation of this signal has been carried out on the basis of the following sets of magnetically equivalent nuclei: three couples of hydrogens, two couples of nitrogens and a group of six protons, as evidenced by the data collected in Table 1, where the hfcc values (in Gauss) reported in the “EXP” line have been used for the spectrum simulation. DFT calculations were carried out combining the B3LYP [20] and PBE0 [21] hybrid functionals with different basis sets; to facilitate the comparison between these values with those arising from experiment, two mean absolute deviation (MAD) [22] values have been computed, i.e. including



Scheme 1. The reversible mono-electronic reduction of DCMV<sup>++</sup>.

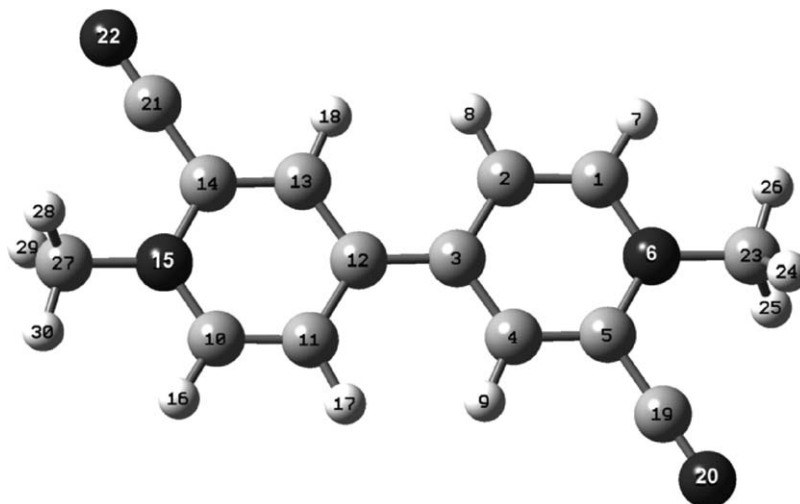


Fig. 1. The *ball and stick* representation of DCMV<sup>•+</sup> PBE0/6-31G(d) optimized geometry showing the arbitrary atom labelling.

Download English Version:

<https://daneshyari.com/en/article/1236428>

Download Persian Version:

<https://daneshyari.com/article/1236428>

[Daneshyari.com](https://daneshyari.com)