ANOMALOUS *g*-FACTORS OF THE DIPHENYLACETYLENE AND DIPHENYLDIACETYLENE ANION RADICALS*

I. B. GOLDBERG and A. J. BARD

Department of Chemistry, The University of Texas at Austin, Austin, Texas 78712, USA

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The *g*-factors of the diphenylacetylene and diphenyldiacethylene anion radicals were measured and found to be 2.00264 and 2.00216 respectively. The unexpected difference between these values is explained by interaction of the phenyl groups with the acetylene p-orbitals.

1. INTRODUCTION

Electron spin resonance spectra of the diphenyl acetylene (DPA) [1, 2, 3, 5] and the diphenyl diacetylene (DPDA) [6] anion radicals have been presented in the literature. The chemical behavior of solutions of the DPA anion radical [4, 5]

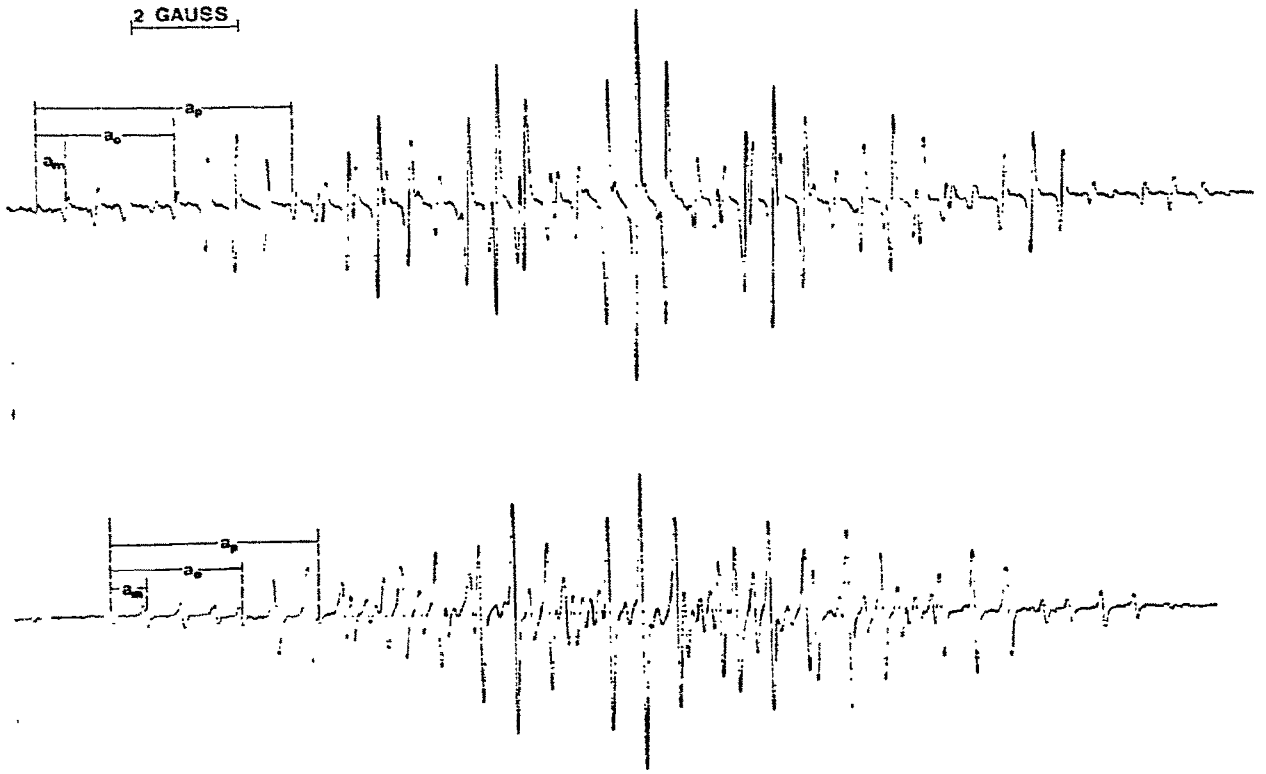

Fig. 1. ESR spectra of diphenylacetylene (upper) and diphenyldiacetylene (lower) prepared by reduction with sodium in 1, 2-dimethyloxyathane at -70° C.

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has also been of recent interest. In the acetylene molecule the acetylene bond is usually considered to be cylindrically symmetric, but little consideration has been given to the perturbing effect of the phenyl groups in the substituted acetylenes. Any variation of the g-factor of these radicals from those containing only sp^2 hybridization may reflect the influence of the difference in electronic structure. We report here the unusually small value for the g-factor of the DPDA anion radical and offer tentative explanation for this effect.

2. EXPERIMENTAL

Samples were prepared by sodium reduction of the hydrocarbon in 1,2-dimethoxyethane (DME). Spectra were obtained with a modified V-4502 spectrometer equipped with a 9 inch magnet and a dual cavity. The sample field was modulated at 100 kHz and the reference field at 7 kHz. A sample of perylene radical anion was used to calibrate the magnetic field [7]. A second sample of perylene radical anion was placed in the sample cavity to determine the field difference between cavities for each measurement of the g-factor [9]. The resonance center occured at a magnetic field of 3330 G at a frequency of 9.325 GHz. The difference between the resonance center of the perylene anion and the hydrocarbon was reproduceable to within 15 mG for each series of measurements. Second order shifts were computed for each compound; however, these cor- corrections were smaller than the uncertainty in the measurements and were, therefore, neglected. As a test of this system, g-factors of anthracene and napthalene anion radicals were measured and found to agree to published values [8, 9] to within 0.7×10^{-15} units.

3. RESULTS

ESR spectra of DPA$^{\dot{-}}$ and DPDA$^{\dot{-}}$ are shown in fig. 1 and the hyperfine splittings are given in table 1. Agreement with values obtained previously is excellent. Spectra of trans-stilbene (TS) [1] and 1,4-diphenyl-1,3- butadiene (DPB) [6] radical anions obtained in this laboratory can be analyzed in terms of the hyperfine splittings presented in the literature.

The g-factors of DPA$^{\dot{-}}$, DPDA$^{\dot{-}}$, TS$^{\dot{-}}$, DBP$^{\dot{-}}$ and 9,10-bis (phenylethynyl) anthracene‡ were

Table 1
Hyperfine splittings (in gauss) for radical anions of diphenylacetylene and diphenyldiacetylene in 1,2-dimethoxyethane

	a_o	a_m	a_p
Diphenylacetylene$^{\dot{-}}$			
K$^+$, -60°C, ref. [1]	2.64 ± 0.03	0.56 ± 0.03	4.82 ± 0.03
Na$^+$, -70°C, this work	2.66 ± 0.02	0.57 ± 0.01	4.88 ± 0.02
Diphenyldiacetylene			
K$^+$, -70°C, ref. [6]	2.47 ± 0.03	0.67 ± 0.03	3.96 ± 0.03
Na$^+$, -70°C, this work	2.47 ± 0.02	0.66 ± 0.01	3.97 ± 0.02

Table 2
g-factors of radical anions

Radical	g a)	$(g-g_e) \times 10^3$ b)	Temp ($^\circ$C)
perylene$^{\dot{-}}$ [8]	2.00267		+25 to −80
diphenylacetylene	2.00264	+0.32	−30 to −80
diphenyldiacetylene	2.00216	−0.19	−60 to −80
9,10-bis (phenylethynyl) anthracene	2.00263	+0.31	−35 to −70
trans-stilbene	2.00270	+0.38	−30 to −70
1,4-diphenyl-1,3-butadiene	2.00270	+0.38	−30 to −70

a) Using perylene cation radical as reference; uncertainty in measured g-factor about $\pm 1 \times 10^{-5}$.
b) free electron g-factor, g_e is 2.00232.

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‡ The ESR spectrum of this anion radical will be reported in detail elsewhere.

measured and are presented in table 2. Several interesting comparisons may be pointed out. The g-factors of DPB$^{\dot{-}}$ and TS$^{\dot{-}}$ have approximately the values which are expected for planar π-conjugated orbitally non-degenerate aromatic hydrocarbon radical anions [8, 9] i.e., between 2.00266 and 2.00272. The g-factor of DPA$^{\dot{-}}$ is slightly smaller than might be expected. However, the g-factor of DPDA$^{\dot{-}}$ is much smaller than would normally be expected and indeed is smaller than the free electron g-factor. Since the g-factor of 9,10-bis (phenylethynyl) anthracene is about that of DPA$^{\dot{-}}$, the small g-factor of DPDA$^{\dot{-}}$ can be attributed to the two adjacent acetylene groups.

4. DISCUSSION

Several mechanisms have been proposed to account for deviations of the g-factor of radicals from that of the free electron (g_e). Stone [10] and O'Reilly and Anderson [11] have shown that the sign of g-g_e in π-conjugated radicals depends upon the balance between two types of excited state which may mix with the ground state of the radical. An excited state which promotes the unpaired electron from a π orbital to a σ^* orbital contributes a decrease to the average g-factor whereas an excited state which promotes an electron from a filled σ-orbital to the unfilled π orbital contributes an increase to the average g-factor. In aromatic radicals the g-factor is usually slightly larger than g_e, indicating that the second effect is more dominant. Two isoelectronic radicals which exhibit in solution g-factors less than g_e are the nitrosobenzene cation radical [12] ($g = 2.0007$) and the benzoyl radical [13] ($g = 2.0014$). The unpaired electron in these radicals, however, is localized in the σ orbitals to a large extent. They are also characterized by large meta-hydrogen splittings and small ortho-and para-hydrogen splittings from the phenyl group. In these cases the promotion of an spin electron to the "empty" π orbital may give use to a negative value of g-g_e.

Hyperfine splittings of DPA$^{\dot{-}}$ and DPDA$^{\dot{-}}$ indicate that the unpaired electron is in a π orbital which is delocalized over the entire system; the small meta-proton splittings and large ortho- and para-hydrogen splittings are evidence for this. The lack of delocalization of the unpaired electron onto the p-orbitals which are orthogonal to the π-electron system indicates that the energy of the lowest antibonding π-orbital of the acetylene anions are nearly equal to those of the analogous, equally substituted ethylene derivative. Evidence which supports this conclusion is that the half-wave reduction potentials of TS has been reported as -1.64 V and that of DPA as -1.69 V versus a mercury pool in dimethylformamide [15]. Since the energies are similar, the difference in the contributions of the sp and sp^2 hybrid orbitals to the g-factors of acetylene and ethylene would not be expected to be significant based on models described earlier [10, 11]. Another factor which must be considered in unquenched angular momentum about the acetylene carbon nucleii due to the two orthogonal p-orbitals. In this case a comparitively simple theory can be involved for this explanation.

Stone [10] has shown that the g-factor may be considered to be approximately the sum of contributions from different atoms or groups of atoms. Carrington and McLachlan [14] and O'Reilly and Anderson [11] present simple calculations of g-factors of atoms in which the unpaired electron is in a p-orbital which is perturbed by some field. A case which may represent an acetylene carbon atom where phenyl substitution exerts a perturbation to alter the degeneracy of the acetylene is one in which the p_z orbital, which is considered to be in the π-conjugated system, is the lowest energy orbital. The orthogonal p_y orbital may be considered to be at a higher energy, and the p_x orbital, which is involved in hybridization, is at such a high energy that it contributes little to the g-factor. The contribution to the difference g-g_e for an acetylene carbon is given by second order perturbation theory

$$g_{xx} - g_e = -\frac{2\zeta}{E_y - E_z} \langle p_z | l_x | p_y \rangle \langle p_y | l_x | p_z \rangle \quad , \tag{1}$$

where g_{xx} is the x component of the g-factor, ζ is the spin orbit coupling constant, and E_y and E_z are the energies of the p_y and p_z orbitals. Evaluation of the matrix elements of eq. (1) gives the result

$$g_{xx} - g_e = -\frac{2\zeta}{E_y - E_z} \; . \tag{2}$$

The z and y components of the g-tensor, g_{zz} and g_{yy}, remain equal to g_e. Eq. (2), therefore, indicates that a negative g-g_e would be expected. Upon consideration of the other contributions in these radicals, eq. (2) would indicate that the g-factor of the acetylene radicals would be lower than one in which there can be no significant contribution from orthogonal p-orbitals, e.g., the analogous ethylene radical, but not necessarily smaller than g_e.

It is difficult to calculate the contribution from each of the acetylene atoms quantitatively since molecular orbitals may not represent the spin density distribution in these radicals. A change in the Hückel molecular orbital parameters of the atoms or bonds in the acetylene group results in a very large change of the calculated unpaired densities on the acethylene atom and the atom on the phenyl group adjacent to the acetylene groups in both DPA$^-$ and DPDA$^{\dot{-}}$, while the unpaired electron density on the remaining phenyl atoms changes slightly. Since we were unable to assign ^{13}C splittings in our spectra, we could not determine the most suitable parameters for the molecular orbital assignment.

The fact that the difference between g-factors of DPA$^{\dot{-}}$ and TS$^{\dot{-}}$ is about 6×10^{-5}, while the difference between those of DPDA$^{\dot{-}}$ and DPB$^{\dot{-}}$ is 57×10^{-5} can be explained in two ways. The first explanation would be that the contribution to eq. (2) from the four acetylene atoms of DPDA$^{\dot{-}}$ must be ten times greater than that from the two acetylene atoms of DPA$^{\dot{-}}$. This would require much greater unpaired electron density in the four acetylene regions of DPDA$^{\dot{-}}$ than DPA$^{\dot{-}}$. Because the hyperfine splittings of these radicals are not significantly different, it is unlikely that this is the entire explanation. A second explanation is that the denominator of eq. (2) is smaller for some of the DPDA$^{\dot{-}}$ acetylene atoms than for the DPA$^-$ acetylene atoms. This would require that the energies of the p_y orbitals of DPDA$^{\dot{-}}$ are lower than those of DPA$^{\dot{-}}$. This can occur in either of two ways: 1. the field exerted by the phenyl group on the inner acetylene carbon atoms of DPDA$^{\dot{-}}$ is smaller, making E_y and E_z more nearly equal for these two atoms or 2. the increased delocalization of the electrons on the p_y orbitals of the four acetylene carbons of DPDA$^{\dot{-}}$ lowers the energy of the p_y orbitals to a much larger extent than delocalization over the two p_y orbitals of DPA$^{\dot{-}}$. We have attempted to prepare radical anions of phenylalkylacetylenes which could permit evaluating the relative effects of these mechanisms, but we have not been successful.

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