vestigators have reported that homocysteine is radioprotective,[26] while others have found it to be nonprotective.[27] Further studies of compounds of this type, including unsymmetrical disulfides, are in progress.

Acknowledgments. The author wishes to thank Professor W. F. Forbes of Waterloo University for stimulating discussions. Thanks are also extended to Mr. R. A. Gravelle for technical assistance throughout.

---

[26] (a) H. Langendorff, R. Koch, and H. Sauer, *Strahlentherapie*, **93**, 281 (1954); (b) P. Alexander, Z. M. Bacq, S. F. Cousens, M. Fox, A. Herve, and J. Lazar, *Radiation Res.*, **2**, 392 (1955).

[27] J. Doull, V. Pizak, and S. J. Brois, University of Chicago, USAF Radiation Laboratory, Status Report No. 62-29, 1962.

Study of the Radical Anion Formation of Some Diphenylacetylenes in Dimethylformamide[1]

R. E. Sioda, D. O. Cowan, and W. S. Koski

Contribution from the Department of Chemistry, The Johns Hopkins University, Baltimore, Maryland 21218. *Received June 27, 1966*

Abstract: The polarographic reduction and the esr investigation of the radical anions of diphenylacetylene, *o*-, *m*-, *p*-methyldiphenylacetylenes, *p,p'*-dimethyldiphenylacetylene, *p*-methoxydiphenylacetylene, *p*-nitrodiphenylacetylene, and 1-naphthylphenylacetylene in dimethylformamide solution were carried out. The cases of the reduction of diphenylacetylene and *p*-nitrodiphenylacetylene are discussed in detail. Sufficiently intense and well-resolved esr spectra were obtained for diphenylacetylene, *p,p'*-dimethyldiphenylacetylene, and *p*-nitrodiphenylacetylene radical anions, permitting a satisfactory interpretation and assignment of the splitting constants. The Hückel and McLachlan MO methods were used to calculate the unpaired spin densities. Good agreement was obtained between experimental and calculated results.

Aromatic hydrocarbons and their derivatives in general produce relatively stable free radical anions on electrolytic reduction in aprotic solvents. It was of interest to us to extend such anion production to acetylenic compounds. A study of the literature shows that, with the exception of the work on the electrolytic reduction of diphenylacetylene reported by Wawzonek and Wearring,[2] no such investigations have been reported on other acetylenic compounds. We have therefore carried out the electrolytic reduction of a series of diphenylacetylene derivatives in dimethylformamide solution and used electron spin resonance (esr) to characterize the resulting free radical anions. With the aid of spin densities estimated from molecular orbital calculations, a reasonable interpretation of the esr spectra was realized, and experimentally consistent values of the molecular orbital integral parameters for the acetylenic bond were established.

Experimental Section

The esr spectra were recorded with a Varian spectrometer using 100-kc field modulation, a 6-in. magnet, and a variable-temperature accessory. Magnetic field measurements were made with a Harvey-Wells nmr precision gaussmeter.

The radical anions were generated inside of the resonance cavity in a manner similar to that reported by Geske and Maki.[3] The description of the cell used has been published previously.[4] A mercury cathode was used in the reductions. The potentials at which the reductions were carried out were chosen from the polarographic half-wave potentials, taking into account the potential drop calculated from the known resistance of the electrolytic cell. A solution of 0.03 *M* tetra-*n*-butylammonium iodide in dimethylformamide was used as a supporting electrolyte.

The polarographic determinations were made with a Sargent-Heyrovský polarograph. The polarographic capillary had a droptime of 5.1 sec for an open circuit and flow rate of 1.281 mg/sec in dimethylformamide when the mercury column height was 45 cm. The half-wave potentials ($E_{1/2}$) were measured using a saturated calomel electrode (sce) as a reference. Special precautions were taken to avoid leakage of the water solution from the calomel electrode to the electrolytic cell.

The oscillopolarographic current *vs.* potential curves[5,6] at various frequencies were displayed on a Tektronix 514 AD oscilloscope. A Hewlett-Packard 202A low-frequency function generator was used as a variable frequency triangular wave source. All the polarographic measurements were made at room temperature (22°).

The dimethylformamide employed was Fisher's infrared spectranalyzed chemical grade which was further purified by drying over anhydrous potassium carbonate followed by distillation at reduced pressure (20 mm).[7] The tetra-*n*-butylammonium iodide was obtained from Eastman Kodak Co. and further purified by recrystallization. The *cis,sym*-diphenylethylene was obtained from the City Chemical Corp. The *trans,sym*-diphenylethylene and diphenylacetylene were used from an older stock and freshly recrystallized. The diphenylacetylene derivatives were prepared by the method of Stephens and Castro.[8] This method consists of heating an equal molar mixture of cuprous phenylacetylide or cuprous *p*-methylphenylacetylide with various *ortho*-, *meta*-, or *para*-substituted iodobenzenes in dry pyridine under a nitrogen atmosphere for 8 hr. The reaction mixtures are diluted with water and then extracted with ether. The crude acetylenes were recrystallized from methanol and then sublimed. The melting points were as follows: diphenylacetylene, 59.5–61.4° (reported value 59–60°); *p*-, *m*-, and *o*-methyldiphenylacetylenes, 70.9–71.8, 30.2–31.2, and 22.8–23.2°, respectively; *p,p'*-dimethyldiphenylacetylene, 138–138.7°; *p*-methoxydiphenylacetylene, 58–58.8° (reported value 58–59°). The *p*-nitro

---

[1] This investigation was supported in part by Research Grant GM 5144 from the Division of General Medical Sciences, Public Health Service, National Institutes of Health.

[2] S. Wawzonek and D. Wearring, *J. Am. Chem. Soc.*, **81**, 2067 (1959).

[3] D. H. Geske and A. H. Maki, *ibid.*, **82**, 2671 (1960).

[4] R. E. Sioda and W. S. Koski, *ibid.*, **87**, 5573 (1965).

[5] J. Vogel, *Collection Czech. Chem. Commun.*, **21**, 502 (1956).

[6] W. Kemula, Z. Kublik, and R. Cyrański, *Roczniki Chem.*, **36**, 1349 (1962).

[7] W. Kemula and R. Sioda, *J. Electroanal. Chem.*, **7**, 233 (1964).

[8] R. D. Stephens and C. E. Castro, *J. Org. Chem.*, **28**, 3313 (1963).

and the 1-naphthyl derivatives melted at 119–120 and 54.5–55.3°. The reported melting point for the former is 119–120°.

Results

Polarographic Data. The compounds investigated in this study and their polarographic reduction data are given in Table I. The values for *cis*- and *trans,sym*-diphenylethylene, which have been previously measured by Wawzonek, *et al.*,[2,9] have been remeasured in this study and also included in the table. The logarithmic slopes of the diphenylacetylene waves were found to be 0.082 and 0.130 for the first and second waves, respectively. The intensities of the waves depended linearly on the square root of the mercury column height although the line of the first wave did not go through the fiducial point.

Table I. Polarographic Reduction Data for Some Diphenylacetylenes in a Solution of 0.03 *M* Tetra-*n*-butylammonium Iodide in Dimethylformamide at 22°[a]

Compound	First wave $E_{1/2}$	First wave I_d	Second wave $E_{1/2}$	Second wave I_d	Third wave $E_{1/2}$	Third wave I_d
Diphenylacetylene	−2.11	3.8	−2.42	2.1		
p-Methyldiphenylacetylene	−2.16	4.2				
m-Methyldiphenylacetylene	−2.17	3.6	−2.48	2.3		
o-Methyldiphenylacetylene	−2.18	3.5	−2.49	1.8		
p,p'-Dimethyldiphenylacetylene	−2.22	4.0				
p-Methoxydiphenylacetylene	−2.24	4.2				
p-Nitrodiphenylacetylene	−0.89	1.9	−1.48	4.4	−2.24	6.3
cis,sym-Diphenylethylene	−2.07	2.1	−2.36	1.3		
trans, sym-Diphenylethylene	−2.08	2.1	−2.38	1.5		
1-Naphthylphenylacetylene	−1.91	2.2	−2.26	5.3		

[a] $E_{1/2}$ = half-wave potential in volts *vs.* sce; $\Delta E_{1/2} = \pm 0.02$ v; I_d = average diffusion current constant in μa mole^{-1} mg$^{-2/3}$ sec$^{1/2}$; $\Delta I_d = \pm 0.2$.

The oscillopolarographic studies show that, if the frequency of the applied voltage is high enough, an oxidation–reduction cycle is formed for all acetylenic compounds studied at the potentials of the first reduction waves. However, with the exception of the case of *p*-nitrodiphenylacetylene, the oxidation part of the cycle disappears when the frequency of the applied voltage is reduced to approximately 1 cps. A typical polarogram and oscillopolarogram of the diphenylacetylene are presented in Figure 1.

Esr Measurements

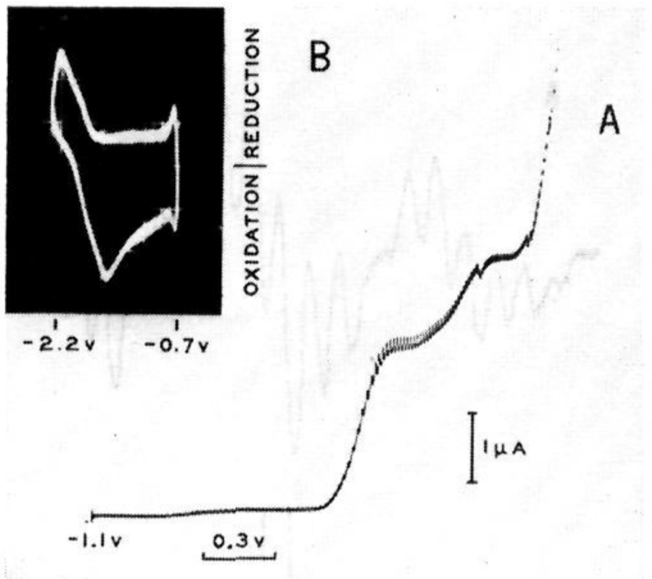


Figure 1. (A) Polarogram of 3.3 × 10^{-4} *M* diphenylacetylene in a solution of 0.03 *M* tetra-*n*-butylammonium iodide in dimethylformamide. (B) Oscillopolarogram of a solution of 10^{-3} *M* diphenylacetylene in the supporting electrolyte; triangular voltage frequency −20 cps.

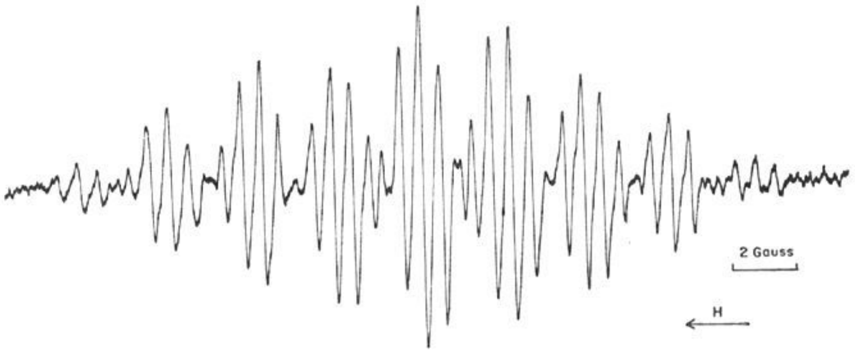


Figure 2. Derivative esr spectrum of the radical anion of diphenylacetylene.

The electroreduction of *p*-nitrodiphenylacetylene at room temperature gave an intense esr spectrum composed of 47 overlapping lines and accompanied by a dark green coloration of the solution near the cathode. Under similar conditions the reduction of the other acetylenic compounds produced weak unresolved esr lines. It was possible, however, to obtain much stronger and better resolved spectra by cooling the solutions to about −50° (the freezing point was about −60°). Persisting purple colorations were formed in these solutions during reduction. The esr spectrum of *p*-nitrodiphenylacetylene was measured at −40 and at 22°, and the splitting constants were the same to within experimental error. Some typical esr spectra are given in Figures 2, 3, and 4, and the splitting constants are tabulated in Table II. The *g* factor of the diphenylacetylene radical anion was found to be 2.0025. The spectrum of the anion *p,p'*-dimethyldiphenylacetylene is given in Figure 4. It consists of 75 apparently equally spaced lines. The equal spacing of the line suggests that the various splitting constants are near multiples of the line spacing. Assuming a line width of 0.25 gauss, a Lorentzian line shape, utilizing a procedure published elsewhere[10] and a program provided us by Professor A. H. Maki, the theoretical spectrum shown in Figure 4 was realized. A Calcomp Plotter Model 570 was used in making this plot. The agreement between the experimental and calculated spacings is good. There is some discrepancy between relative intensities of the lines which presumably could be improved by adjusting the line width or shapes. The values of the experimental splitting constants for three diphenylacetylene derivatives are given in Table II. The values of the splitting constants have been refined by a procedure outlined elsewhere.[11]

---

(9) S. Wawzonek, E. W. Blaha, R. Berkey, and M. E. Runner, *J. Electrochem. Soc.*, **102**, 235 (1955).

(10) E. W. Stone and A. H. Maki, *J. Chem. Phys.*, **38**, 1999 (1963).

(11) J. Reeder, G. Odell, R. E. Sioda, and W. S. Koski, *J. Mol. Spectry.*, **20**, 141 (1966).

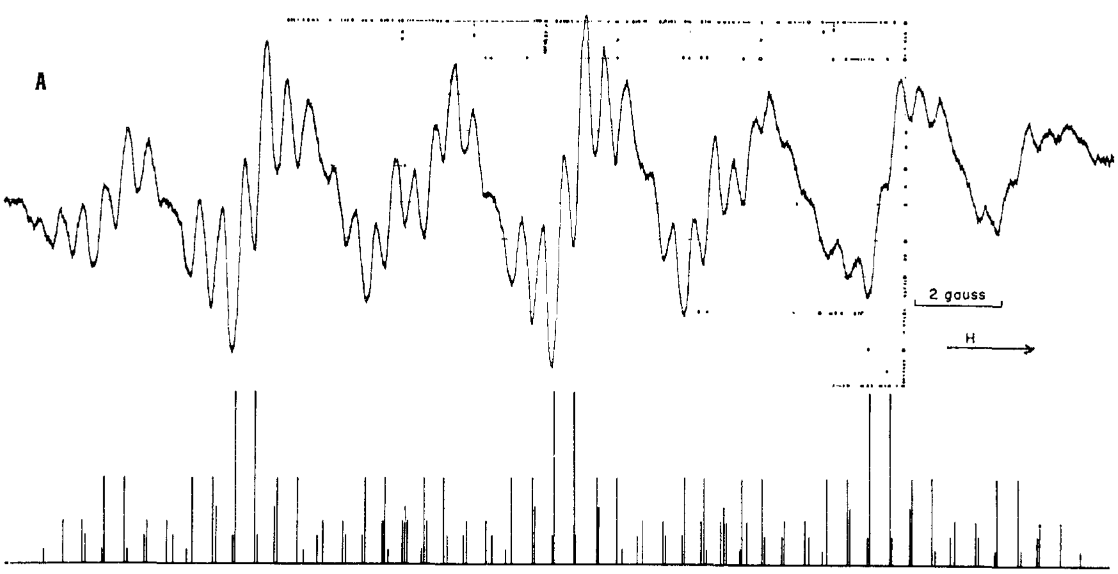


Figure 3. (A) Derivative esr spectrum of the free radical anion of *p*-nitrodiphenylacetylene. (B) Calculated line diagram built from the splittings of Table II.

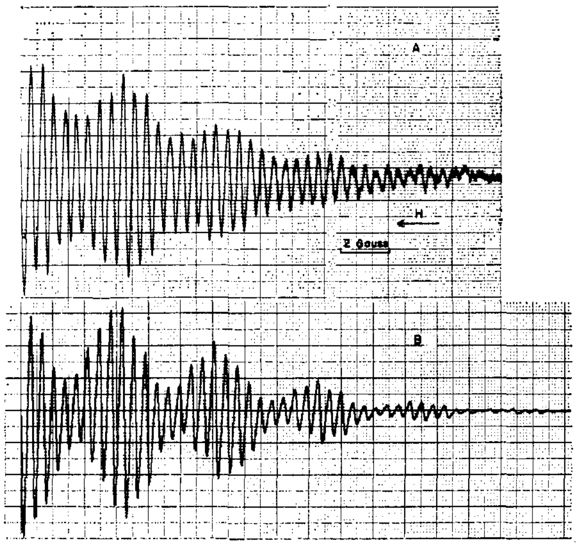


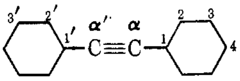
Figure 4. (A) One-half (low-field) of the derivative esr spectrum of the *p,p'*-dimethyldiphenylacetylene radical anion. (B) Calculated spectrum using the splitting constants from Table II and a line width of 0.25 gauss.

Discussion

Reduction Course. In view of the similarity of the results obtained for all of the diphenylacetylene derivatives (Table I) with the exception of *p*-nitrodiphenylacetylene, the discussion will be limited to the parent compound which will be taken as representative. The *p*-nitrodiphenylacetylene will be discussed separately.

Wawzonek and Wearring reported[2] that diphenylacetylene in dimethylformamide was reduced in two one-electron waves with half-wave potentials of −1.69 and −1.96 v *vs.* mercury pool with current constants I_d = 1.92 and 2.3, respectively. It was proposed that the first wave leads to the formation of the diphenylacetylene free radical anion $R + e = R^-$, and the second leads to its reduction to form R^{-2}. The significant differences obtained in this study suggest that a modified mechanism should be considered for the process. Examination of the results in Table I show that the diffusion constants for diphenylacetylene and its derivatives range from 3.5 to 4.2 which are considerably larger than the value of 1.92 reported for diphenylacetylene.[2] Since the value of a one-electron reduction of an aromatic hydrocarbon is usually close to 2 μa mole^{-1} mg$^{-2/3}$ sec$^{1/2}$, the results obtained in this study correspond more closely to a two- rather than a one-electron reduction process. Furthermore, the absence of strong esr signals during the course of the room-temperature reduction indicates that the radical anions formed are not very stable. On the other hand, the half-wave potentials of diphenylacetylene reduction waves obtained in this study agree well with those reported by Wawzonek, *et al.*,[2] especially if the potential difference of −0.43 v between the Hg pool and the sce is taken into account.

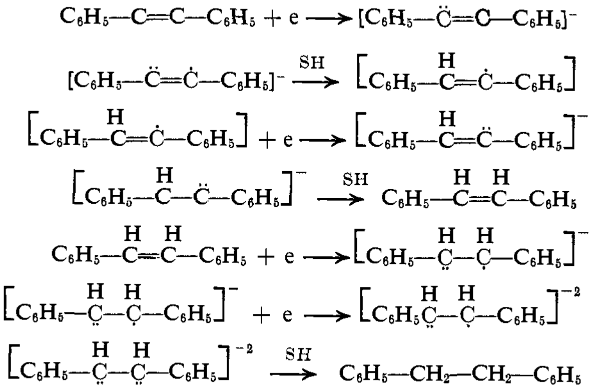
Table II. Experimental Splitting Constants (gauss) Obtained at −40°

Radical anion of	Position	Splitting constant
Diphenylacetylene	2,2'	2.80
	3,3'	0.60
	4,4'	5.08
p,p'-Dimethyldiphenylacetylene	2,2'	3.75
	3,3'	0.92
	CH_3,CH_3'	4.23
p-Nitrodiphenylacetylene	N	8.0
	2	1.0
	3	3.0
	2'	0.6
	4'	0.6

If the reduction of diphenylacetylene is considered to be a two-electron process followed by the addition of two protons, one would expect the formation of one or both of the *sym*-diphenylethylenes. These compounds would be expected to be further reduced to form bibenzyl by another two-electron process. Bibenzyl has been reported as the main product in the electrolysis of diphenylacetylene.[2] The similarity of the half-wave potentials of diphenylacetylene and the *sym*-diphenylethylenes (see Table I) also favors this assumption.

Two mechanisms, A and B, suggest themselves for the reduction of acetylenic compounds, and both of them follow the general outline for the reduction of hydrocarbons proposed by Hoijtink, *et al.*[12] In mechanism A the mononegative ion reacts with a proton source to form a neutral radical, and this radical in turn promptly adds another electron.[12] The presence of a chemical (kinetic) part in the first stage of the reduction of diphenylacetylene is supported by the irreversibility of its first wave and the fact that the plot of the wave intensity *vs.* the square root of the Hg column height does not go through the fiducial point. These kinetic effects will also reduce the current expected for an over-all addition of three electrons if the *sym*-diphenylethylene free radical anion was the main product in this wave (sequence 1–5). The relatively rapid reaction of the negative ion with a proton source (eq 2) is also consistent with the fact that the oxidation part of the oscillopolarographic cycle disappears when the frequency of the applied alternating voltage is low. This mechanism appears to explain the instability of the free radical anion of diphenylacetylene and the near two-electron height of its reduction wave.

Mechanism A



$$C_6H_5{-}C{=}C{-}C_6H_5 + e \longrightarrow [C_6H_5{-}\ddot{C}{=}C{-}C_6H_5]^- \quad (1A)$$

$$[C_6H_5{-}\ddot{C}{=}\dot{C}{-}C_6H_5]^- \xrightarrow{SH} \left[C_6H_5{-}\overset{H}{C}{=}\dot{C}{-}C_6H_5\right] \quad (2A)$$

$$\left[C_6H_5{-}\overset{H}{C}{=}\dot{C}{-}C_6H_5\right] + e \longrightarrow \left[C_6H_5{-}\overset{H}{C}{=}\ddot{C}{-}C_6H_5\right]^- \quad (3A)$$

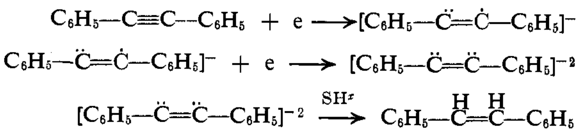
$$\left[C_6H_5{-}\overset{H}{C}{-}\ddot{C}{-}C_6H_5\right]^- \xrightarrow{SH} C_6H_5{-}\overset{H}{C}{=}\overset{H}{C}{-}C_6H_5 \quad (4A)$$

$$C_6H_5{-}\overset{H}{C}{=}\overset{H}{C}{-}C_6H_5 + e \longrightarrow \left[C_6H_5{-}\overset{H}{\underset{\cdot\cdot}{C}}{-}\overset{H}{\underset{\cdot}{C}}{-}C_6H_5\right]^- \quad (5A)$$

$$\left[C_6H_5{-}\overset{H}{\underset{\cdot\cdot}{C}}{-}\overset{H}{\underset{\cdot}{C}}{-}C_6H_5\right]^- + e \longrightarrow \left[C_6H_5\overset{H}{\underset{\cdot\cdot}{C}}{-}\overset{H}{\underset{\cdot}{C}}{-}C_6H_5\right]^{-2} \quad (6A)$$

$$\left[C_6H_5{-}\overset{H}{\underset{\cdot\cdot}{C}}{-}\overset{H}{\underset{\cdot\cdot}{C}}{-}C_6H_5\right]^{-2} \xrightarrow{SH} C_6H_5{-}CH_2{-}CH_2{-}C_6H_5 \quad (7A)$$

Mechanism B



$$C_6H_5{-}C{\equiv}C{-}C_6H_5 + e \longrightarrow [C_6H_5{-}\ddot{C}{=}\dot{C}{-}C_6H_5]^- \quad (1B)$$

$$C_6H_5{-}\ddot{C}{=}\dot{C}{-}C_6H_5]^- + e \longrightarrow [C_6H_5{-}\ddot{C}{=}\ddot{C}{-}C_6H_5]^{-2} \quad (2B)$$

$$[C_6H_5{-}\ddot{C}{=}\ddot{C}{-}C_6H_5]^{-2} \xrightarrow{SH^x} C_6H_5{-}\overset{H}{C}{=}\overset{H}{C}{-}C_6H_5 \quad (3B)$$

Steps 4–6 same as in mechanism A

Mechanism B would predict a current constant for the first reduction wave of diphenylacetylene corresponding to either something greater than that expected for a two-electron process (reactions 1–4) or to a one-electron process (reaction 1). The latter possibility is probably more likely since the negative charge of the anion would lower the tendency of an immediate formation of a dinegative anion and thus increase the electrolytic potential of its occurrence.

It is, of course, possible that both reaction mechanisms A and B are operative. The above reasoning, coupled with the fact that the esr spectra of the anions are considerably improved as the temperature is lowered because of the reduction in reaction rate with proton donors, suggests that mechanism A is the dominant one.

In contrast to the other diphenylacetylene derivative, *p*-nitrodiphenylacetylene forms a one-electron reduction wave at −0.89 v. This corresponds to the formation of a free radical anion in green colored solution whose esr spectrum is shown in Figure 3. Further reduction takes place at −1.48 v, and, in analogy with the usual course of reduction of aromatic nitro compounds in dimethylformamide,[7,13] three more electrons with four protons are probably added to form *p*-hydroxyaminodiphenylacetylene. The acetylenic bond is reduced only at the negative potential of −2.24 v.

Esr Spectra

The esr spectrum of diphenylacetylene free radical anion has been previously studied by Zhuravleva, *et al.*[14] It was produced by the reaction of sodium metal with diphenylacetylene in tetrahydrofuran. The limited resolution of the spectrum permitted an evaluation of only two splitting constants of 1.67 ± 0.27 and 2.8 ± 0.46 gauss for the *ortho* and *para* hydrogens, respectively. The values obtained in this study are significantly higher, corresponding to splitting constants of 2.80 and 5.08 gauss for the *ortho* and *para* positions, respectively. The spectrum also permitted the evaluation of a *meta* position constant of 0.60 gauss. The reasons for these disagreements are not clear to us.

In view of the reduction mechanism proposed in this study, it is interesting to note that the spectrum measured here and also the one measured by Zhuravleva, *et al.*, do not resemble the radical spectrum obtained from 1,2-diphenylethylene by electroreduction.[15] Consequently, the discrepancy noted between these two studies does not arise from contributions from diphenylethylene radical anions.

A typical esr spectrum of *p*-nitrodiphenylacetylene radical anion is shown in Figure 3. An easily discernible nitrogen triplet further split by protons is observed. It will be noted that the lines corresponding to nitrogen splitting on the high-field side are considerably broader than the corresponding lines on the low-field side. Such broadening has been previously reported[16] in several nitro aromatic radical anions and has been attributed to molecular tumbling modulation of the intramolecular anisotropic dipolar and *g*-tensor interactions. The splitting constants that were evaluated for this radical are given in Table II.

Calculated and Experimental Spin Densities

The Hückel and McLachlan[17] calculations of the unpaired spin densities have been carried out for compounds investigated in this study. With the exception of a paper by Streitwieser on ionization potentials[18] and an article by Zhuravleva, *et al.*,[14] we are not aware of any molecular orbital calculation published on

---

(12) G. J. Hoijtink, J. van Schooten, E. de Boer, and W. I. Aalbersberg, *Rec. Trav. Chim.*, 73, 363 (1954).

(13) W. Kemula and R. Sioda, *Bull. Acad. Polon. Sci., Ser. Sci. Chim.*, **10**, 107 (1962).

(14) T. S. Zhuravleva, E. S. Petrov, and D. N. Shigorin, *Zh. Strukt. Khim.*, **5**, 785 (1964).

(15) R. Chang and C. S. Johnson, *J. Chem. Phys.*, **41**, 3272 (1964).

(16) J. H. Freed and G. K. Fraenkel, *ibid.*, **39**, 326 (1963); **40**, 1815 (1964).

(17) A. D. McLachlan, *Mol. Phys.*, **1**, 233 (1958).

(18) A. Streitwieser, Jr., *J. Am. Chem. Soc.*, **82**, 4123 (1960).

acetylenic compounds. Consequently, there is some uncertainty in the molecular orbital parameters for the acetylenic carbons. We have therefore examined a complete range of values of 1.0–2.0 for $K_{\alpha-\alpha}$ and -0.5–1.5 for h_α, striving for the best fit of the calculated and experimental spin densities. $K_{\alpha-\alpha}$ is the resonance integral parameter in the equation: $\beta_{\alpha-\alpha} = K_{\alpha-\alpha}\beta_0$ and h_α is the Coulomb integral parameter in the equation $\alpha_\alpha = \alpha_0 + k_\alpha\beta_0$, where β_0 is the resonance integral of an aromatic carbon–carbon bond and α_0 is the Coulomb integral of an aromatic carbon. The best general correlation of the spin densities was found for $K_{\alpha-\alpha}$ = 1.4 and for $h_\alpha = -0.4$. In the case of the ionization potential calculations, Streitwieser used $K_{\alpha-\alpha}$ = 1.38 and h_α = 0.[18] For the nitro group, the parameters of Rieger and Fraenkel[19] were used; and for the methyl group, the heteroatom and the inductive models have been employed additively with $K_{\text{C-CH}_3} = 0.7$ and $h_{\text{CH}_3} = 2.0$ and $k_{\text{C(-CH}_3)} = -0.5$.[20] In all of the calculations, the parameter λ of the McLachlan procedure was kept equal to 1.2.

The Hückel molecular orbital calculation of diphenylacetylene gave 14 energy levels of which the seven lowest were occupied by 14 π electrons in the neutral compound. The second acetylenic π electron pair lies in the plane of the molecule and is assumed not to participate in the filling of the above molecular orbitals. During the formation of the radical anion, the additional electron enters the first antibonding orbital of MO energy $0.7226\beta_0$. For *p,p'*-dimethyldiphenylacetylene and *p*-nitrodiphenylacetylene, the nine lowest orbitals are occupied in the neutral compound by 18 π electrons (two methyl groups and the nitro group donate 4 π electrons to the system). The MO energies of the first antibonding orbitals are $0.8876\beta_0$ and $0.3785\beta_0$ for the dimethyl and nitro derivatives, respectively.

The theoretical and experimental spin densities are given in Table III. The experimental spin densities were calculated from the splitting constants (Table II) by the McConnell relationship[21]

$$a^{\text{H}}_{\text{i}} = Q^{\text{H}}_{\text{CH}}\rho^{\pi}_{\text{i}}$$

where $Q^{\text{H}}_{\text{CH}} = -23.7$ gauss in accordance with the suggestion of Karplus and Fraenkel.[22] For the methylenic protons, $Q^{\text{H}}_{\text{C-CH}_3} = 27.2$ gauss was used.[22]

Table III. Calculated and Experimental Spin Densities

Radical anion	Position	Spin densities Calculated[a] Hückel	 McLachlan	 Exptl
Diphenylacetylene	1	0.104	0.111	. . .
	2	0.071	0.083	0.118
	3	0.017	−0.020	0.025
	4	0.170	0.174	0.214
	α	0.090	0.089	. . .
p,p'-Dimethyldiphenylacetylene	C (methyl)	0.006	0.007	. . .
	1	0.091	0.090	. . .
	2	0.090	0.117	0.158
	3	0.001	−0.044	0.039
	4	0.110	0.146	0.155[b]
	α	0.110	0.094	. . .
p(4)-Nitrodiphenylacetylene	O	0.168	0.176	. . .
	N	0.191	0.204	. . .
	1	0.112	0.146	. . .
	2	0.008	−0.036	0.043
	3	0.090	0.119	0.127
	4	0.041	0.017	. . .
	1'	0.006	−0.001	. . .
	2'	0.018	0.025	0.024
	3'	0.001	−0.008	. . .
	4'	0.021	0.026	0.024
	α	0.003	−0.021	. . .
	α'	0.056	0.074	. . .

[a] The calculations of the theoretical unpaired spin densities have been performed on IBM 7040 and 7094 digital computers using special Hückel and McLachlan programs. [b] Calculated from the *methyl*-proton splitting (see text).

The *ortho* and *meta* hydrogen splitting constants of *p*-nitrodiphenylacetylene radical anion, 3.02 and 1.03, respectively, show considerable similarity to the corresponding values of 3.36 and 1.07 in the nitrobenzene anion.[19] The nitrogen splitting constant of *p*-nitrodiphenylacetylene anion is smaller than in the nitrobenzene anion (8.03 compared to 9.70). It correlates well with the theoretical value of 7.7 gauss calculated according to the equation of Rieger and Fraenkel.[19]

After completion of this manuscript, the paper of Broadhurst and Warhurst[23] on the esr spectrum of the diphenylacetylene anion radical came to our attention. The spectrum and splitting constants reported by them agree with the results obtained in this study.

Acknowledgment. The authors thank Mr. D. Saperstein and Mr. G. Odell for their help in the computational part of this paper. We also thank Professor Ph. H. Rieger for sending us his copy of the McLachlan program, and Professor A. H. Maki for a copy of the SESRS (Simulation of ESR Spectra) program.

---

(19) Ph. H. Rieger and G. K. Fraenkel, *J. Chem. Phys.*, **39**, 609 (1963).

(20) A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," John Wiley and Sons, Inc., New York, N. Y., 1961, p 135.

(21) H. M. McConnell, *J. Chem. Phys.*, **24**, 764 (1956).

(22) M. Karplus and G. K. Fraenkel, *ibid.*, **35**, 1312 (1961).

(23) J. G. Broadhurst and E. Warhurst, *J. Chem. Soc., Sect. A*, 351 (1966).