The fit we managed to obtain is shown in Figure 1.

Voltammograms were digitized by using a Textronix 4953 graphics tablet attached to the Chemistry Department HARRIS/7 computer. The experimental CV curve was subtracted from a background scan and the resulting digitized curve transferred to an IBM PC. The simulated curve was matched to the experimental trace by scaling the simulated maximum to the experimental maximum in the current dimension and by offsetting the zero point of the simulation by the voltage offset used in the simulation.[24] For the data simulated, the scan range was 0.7 V and the starting potential was 0.337 V negative of $E^{\circ\prime}{}_1$, so the starting potential for the simulation was −0.337 V and the switching point 0.363 V. The peak current in the simulation was normalized to that of the experimental data. The ratios of heterogeneous electron-transfer rate from the substrate to the electrode and from the electrode to the substrate were taken to be 1; i.e., $\alpha$ was set at 0.5 for all species. The peaks are both broad, and all $\psi$ values (which describe the broadening of the peaks induced by slow heterogeneous electron transfer rates) were set at 0.3. The parameters used for the simulation in Figure 1 (see Scheme III for the reactions referred to) were $E^{\circ\prime}{}_2 - E^{\circ\prime}{}_1 = 0.135$ V (reactions 1 and 2), rate 3 = 59 $s^{-1}$, $K_{eq}$ 4 = 6, $E^{\circ\prime}{}_1 - E^{\circ\prime}(B^+) = 0.2$ (reaction 6, a larger value did not affect the simulation), rate 8 = 2 $M^{-1}\,s^{-1}$, rate 9 = 0.0001 $M^{-1}\,s^{-1}$.

**ESR.** Preparation of the ESR samples of $12^+$, $14^+$, and $16^+$ were accomplished by chemical oxidation. A solution of hydrazine ($2 \times 10^{-3}$ M) was made up in butyronitrile and the solution cooled under nitrogen. Nitrogen was bubbled through the solution for at least 15 min, and 1 equiv of tris(*p*-bromophenyl)amminium hexachloroantimonate was added as the oxidant. A portion of this solution was forced through a cooled cannula into a precooled 3-mm (o.d.) Pyrex tube and kept in dry ice/ethanol until ready for use. Spectra were recorded on a Varian E-15 instrument, and simulations were carried out on an IBM PC, plotted on an HP-7047A digital plotter, and visually compared with the experimental curves.

**Calculations.** MM2 calculations[12] on the hexacyclic and pentacyclic bis(methylamine)s **22** were done on the Chemistry Department HARRIS/7 computer. Calculations on model diamine **24** were done on an IBM PC using a three-part MM2 program supplied by Prof. G. R. Weisman. MNDO calculations[25] were carried out on the Madison Academic Computing Center VAX-780.

**Acknowledgment.** We thank the National Institutes of Health for partial financial support under Grant GM-29549. We thank SERC for a studentship (N.M.S.). We thank J. T. Ippoliti for obtaining the high-resolution mass spectral data on **2–4**.

**Registry No.** **2**, 49840-62-2; **3**, 101032-34-2; **4**, 101032-35-3; **5**, 2594-64-1; **7**, 101032-36-4; **8**, 77144-30-0; **11**, 49840-61-1; **12**, 87783-35-5; **13**, 87783-36-6; **14**, 87783-37-7; **16**, 101032-37-5; **17**, 101032-38-6; **18**, 52598-10-4; **19**, 49840-60-0; **20**, 53779-90-1; **21**, 38704-89-1; **22**, 87783-30-0; **24**, 39123-05-2; $Me_2NN{=}CHCHNNMe_2$, 26757-28-8; $Me_2NN(Me)C(O)CH_2C(O)N(Me)NMe_2$, 101032-39-7; $MeNN(Me)C(O)(CH_2)_3C(O)N(Me)NMe_2$, 101054-48-2.

**Supplementary Material Available:** Observed and simulated ESR spectra for $12^+$ and $16^+$ (3 pages). Ordering information is given on any current masthead page.

---

[24] The effects of changing the simulation parameters on the simulated CV curves are discussed in more detail in the thesis of M. R. Willi (University of Wisconsin, 1985). Our lack of success in quantitatively fitting the experimental curves shows that the simulations done were inadequate, and we do not feel that space describing them here is warranted.

---

# Electrochemical Oxidation and Reduction of a Substituted Alkylidenecyclopropanaphthalene[†]

Kevin Ashley, John K. Foley, Qiu Mei, Jamal Ghoroghchian, Fereshteh Sarfarazi, John Cassidy, Brian Halton,[‡] Peter J. Stang, and Stanley Pons*

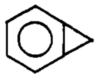
*The Department of Chemistry, University of Utah, Salt Lake City, Utah 84112, and Department of Chemistry, Victoria University of Wellington, Private Bag, Wellington, New Zealand*

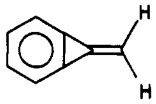
*Received December 4, 1985*

Electrochemical and spectroelectrochemical investigations of 1-(diphenylmethylene)cyclopropa[*b*]naphthalene in dry acetonitrile solutions show the formation of a stable anion radical ($\lambda_{max}$ 519 nm) and cation radical, the first evidence of stable radicals of a methylenecycloproparene structure. Reaction of the radical anion with oxygen occurs at a rate close to the diffusion-controlled limit.

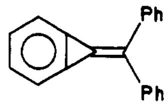
Highly strained molecules have fascinated chemists for over a century due to their unusual properties and reactivity.[1] There is a great deal of current interest and research activity in cycloproparene chemistry. The parent cycloproparene compound I has a strain energy of 68 kcal/mol, which is one of the highest known.[2]

The even more strained and unusual alkylidene derivatives of I have recently been reported.[3] Although the highly strained methylenecycloproparene parent compound II has not been isolated to date, two of us[3] have reported the successful synthesis of the 1,1-diphenyl (III) and the 1-methyl-1-phenyl (IV) derivatives as well as the corresponding naphthalene analogues V and VI. Compound V is stable in air and in aprotic solvents against rapid oxidation. Our initial spectral characterization indicated the possibility of charge-separated resonance forms

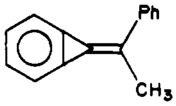

I



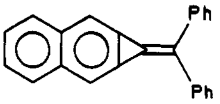
II



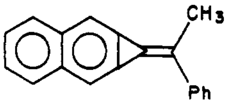
III



IV



V



VI

---

[†] Dedicated to Professor Cheves Walling on the occasion of his 70th birthday.

[‡] Victoria University.

[1] Greenberg, A.; Liebman, J. F. *Strained Organic Molecules*; Academic: New York, 1978.

[2] Halton, B. *Ind. Eng. Chem. Prod. Res. Dev.* **1980**, *19*, 349. Billups, W. E. *Acc. Chem. Res.* **1978**, *11*, 245.

0022-3263/86/1951-2089$01.50/0

contributing to the neutral molecule. In an effort to further understand the structural aspects and the characterization of the new species, we have undertaken an electrochemical and spectroelectrochemical investigation of V.

It will be shown that the molecule forms a stable anion radical and a stable cation radical when electrochemically reduced or oxidized, respectively, in acetonitrile solution containing no oxygen. The anion radical reacts rapidly with oxygen in acetonitrile; the reaction rate appears to be very close to the diffusion limit.

## Experimental Section

**Chemicals and Reagents.** The preparation of V has been described in detail recently.[3] Briefly, naphthocyclopropene is first treated with *n*-butyllithium[4] and chlorotrimethylsilane and then with potassium *tert*-butoxide and benzophenone. The product, after purification, is a stable yellow crystalline solid, mp 110–111 °C. Tetra-*n*-butylammonium tetrafluoroborate (TBAF) was prepared from the metathesis of sodium tetrafluoroborate and tetra-*n*-butylammonium hydrogen sulfate. The crude product was washed with ice water, dissolved in a minimum amount of methylene chloride, and precipitated with cold diethyl ether. After being recrystallized a second time, the product was air dried and stored in a vacuum oven at 75 °C for 24 h before use.

Acetonitrile solvent was HPLC grade (Baker Chemicals, 0.001% nominal water content) and was used as received. Deoxygenation of the reaction mixture was effected by purging with dry helium gas just prior to the experiments.

The electrolyte for the silver wire reference electrode was 0.01 M silver nitrate in 0.10 M TBAF in acetonitrile. All potentials given in this paper are with respect to this electrode.

**Electrochemistry and Spectroelectrochemistry.** Control of the electrode potential was accomplished with a three electrode potentiostat and waveform generator (JAS Instrument Systems, Inc.). The cell held a 7-mm diameter platinum mirror disk electrode and was used both for electrochemical and spectroelectrochemical experiments. The cell contained two quartz optical windows set to effect a 45° angle of incidence for the incident UV/vis radiation. The exact details have been described elsewhere (ref 5 and JAS Instrument Systems, Inc.).

The optical cell was mounted on an optical bench, and radiation from a monochromator (MacPherson Model 302) was reflected from the electrode surface and then onto a photomultiplier (RCA Model 31000A). The signal from the photomultiplier was digitized by an oscilloscope (Tektronix Model 5223), and the data were passed over a GPIB bus to a computer/plotter system (IBM Model 9000). For the spectroelectrochemical transients, the background intensity was controlled so that the value of the absorbance could be calculated as described previously.[5] The potential was initially maintained at a value where no electrochemical reaction was taking place. The potential was then stepped to a value where the diffusion-controlled conversion of the species of interest was initiated, and the spectroelectrochemical absorbance of the electrogenerated species was recorded on a digital oscilloscope as a function of time.

## Results and Discussion

**Voltammetry.** A typical cyclic voltammogram of V at negative potentials is shown in Figure 1a. In dry deoxygenated acetonitrile at a platinum electrode there is a one-electron wave, corresponding to reduction of the neutral molecule to the anion radical. The wave is reversible (the ratio of the cathodic to anodic peak currents is unity, and the peak separation at 100 mV $s^{-1}$ is 60 mV), and the half-wave potential is −1.93 V vs. the $Ag/Ag^+$ reference couple. The radical anion is very stable and shows no signs of decay on the time scale of the voltammetric experiments (1 min). A voltammetric sweep to positive potentials reveals a single electron oxidation of V to its radical cation. The anodic and cathodic peak potentials are independent of sweep rate and are separated by 60 mV, but the anodic peak current is greater than the cathodic peak current. This corresponds to a reversible electron-transfer step (the half-wave potential of which is +0.81 V) followed by slow decomposition of the resulting cation radical, most likely by reaction with residual water. If the potential is swept to negative values immediately after formation of the cation radical, a new peak due to reduction of the decomposition product(s) appears at about −0.8 V. The nature of these reaction products is the subject of continuing work. Voltammetry at more positive potentials reveals an anodic peak at about +1.1 V due to oxidation of the cation radical to the dication. The dication is very unstable—no peak for its reduction can be observed on the reverse sweep. Virtually identical behavior at both positive and negative potentials was observed for V at a glassy carbon electrode.

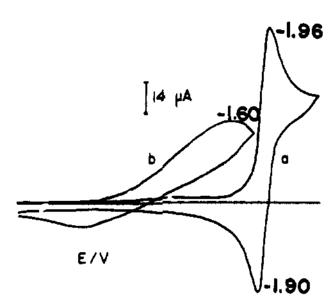
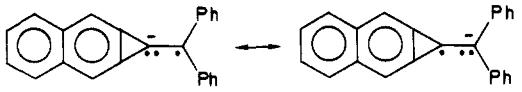
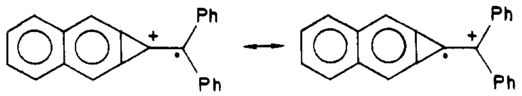


**Figure 1.** Cyclic voltammetry of (a) V and (b) dioxygen in acetonitrile solution at a platinum electrode. The sweep rate was 50 mV/s, the solution in (a) was 1 mM in V, and the potentials are vs. a $Ag/Ag^+$ (0.01 M $AgNO_3$ in 0.1 M TBAF in acetonitrile) reference.

The question of the structures of the ion radicals naturally arises. The reversibility of the oxidation and reduction of V indicates that no ring-opening occurs when the anion radical and cation radical are formed. Compound V is reduced at rather less negative potentials and is oxidized at rather less positive potentials than many other aromatic hydrocarbons in acetonitrile. (The half-wave potential for reduction of V is −1.93 V vs. $Ag/Ag^+$. For tetraphenylethylene this value is −2.5 V, for naphthalene −2.9 V, for anthracene −2.4 V, for diphenylanthracene −2.1 V, for pyrene −2.5 V, and for perylene −2.30 V. The half-wave potential for oxidation of V is +0.81 V. For tetraphenylethylene this value is +1.0 V, for naphthalene +1.40 V, for anthracene +0.91 V, for diphenylanthracene +0.92 V, for pyrene +1.06 V, and for perylene +0.66 V).[9] It seems probable that on formation of the radical ions, the olefinic double bond is broken. The resulting release of strain would reduce the free energy of formation of the ions so that the anion would be formed at less negative potentials and the cation formed at less positive potentials than otherwise expected. Plausible structures for the anion radical would then be



The structure of the cation radical might be



Our electrochemical data do not allow us to conclude for

---

[3] Halton, B.; Randall, C. J.; Stang, P. J. *J. Am. Chem. Soc.* **1984**, *106*, 6108.

[4] Eaborn, C.; Eidenschink, R.; Harris, S. J.; Walton, D. R. M. *J. Organomet. Chem.* **1977**, *124*, C27; **1980**, *193*, 155.

[5] Pons, S.; Khoo, S. B. *J. Am. Chem. Soc.* **1982**, *104*, 3845.

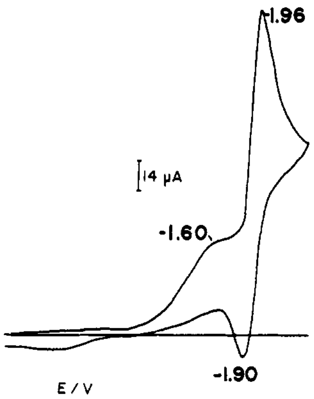


**Figure 2.** Cyclic voltammetry of the mixed system of the components in Figure 1. The system parameters are the same.

either species which resonance structure is the more important.

At a polished platinum mirror disk electrode, the reduction of a blank solution containing the same electrolyte shows no faradaic current over the same range of potentials. If oxygen is admitted to the blank and the voltammetry is investigated at negative potentials, one observes a kinetically slow electron-transfer reaction corresponding to reduction of oxygen to superoxide (Figure 1b). The reduction peak occurs at −1.60 V, and the peak for reoxidation of superoxide to oxygen occurs at −0.78 V. The diffusion-controlled peak for superoxide formation is thus 360 mV less negative than the peak for the reversible formation of the radical anion of V. At a glassy carbon electrode, the oxygen reduction is kinetically more reversible. The reduction peak for superoxide formation is now at −1.30 V, and the corresponding oxidation wave is now at −1.06 V. The voltammetry of the isolated V and oxygen solutions at the platinum electrode shows linear relationships between the peak currents for both formation of the anion radical of V and for superoxide formation with the square root of the sweep rate up to about 500 mV $s^{-1}$. The plots intersect the origin. This is the expected result for electrochemical reactions where there are no complicating chemical reactions involving the reactants or products of the electron transfer reaction, and where there are no complications from the adsorption at the electrode surface of reactants or products of the electron-transfer reaction.

The voltammetry at the platinum electrode of systems containing both V and oxygen is more complicated than that of the individual systems described above (e.g., Figure 2). The first reduction wave I still corresponds to superoxide formation. The magnitude of the current in the second wave II, corresponding to anion radical formation, becomes larger than can be rationalized by the simple one electron-transfer reaction observed in the single component (V) system described above. Several possibilities exist for the explanation of this behavior.

One possibility is the case where an additional electroactive species is formed whose reduction potential is less than that of V. In the case at hand, this would most likely be due to the reaction of the anion radical of V with diffusing oxygen or superoxide.

$$V^{\bullet -} + O_2 \rightleftarrows W$$

$$W + ne^- \rightleftarrows X$$

or

$$V^{\bullet -} + O_2^- \rightleftarrows Y$$

$$Y + ne^- \rightleftarrows Z$$

(The second reaction is energetically unfavorable.) There was, however, no evidence of the expected products of these reactions in exhaustive preparative electrolysis of V at potentials at or negative of its reduction wave. In addition, if such an electrochemical–chemical–electrochemical reaction sequence was taking place here, the height of wave II would imply the involvement of several electrons in the reduction of W or Y. Although this is possible, it is unlikely.

There was no evidence of the irreversible reaction of unreduced V with oxygen, since the uncomplicated voltammetric behavior shown in Figure 1a could be reproduced by simple deoxygenation of the solution with helium purging. In addition, if the negative-proceeding voltammetric sweep was reversed in the mixed system before the second voltammetric wave, the oxidation peak for superoxide was found to be uncomplicated, i.e., identical with Figure 1a. In Figure 2, there is obviously a depletion of available total anion in the diffusion layer (the oxidation peak is greatly reduced in magnitude). This is also evidence that the superoxide ion does not chemically react to any significant extent with V. In all of the above possibilities, a product of V and oxygen should result. Exhaustive electrolysis at potentials at or past the second reduction wave fails to yield significant yields of any product of V except the anion radical.

Another possibility for the unusually high current in the second reduction wave is the catalytic regeneration of V by the subsequent reaction of the anion radical with oxygen to form V and superoxide

$$V^{\bullet -} + O_2 \rightleftarrows V + O_2^-$$

and with superoxide to form V and peroxide

$$HS + V^{\bullet -} + O_2^- \rightleftarrows V + HO_2^- + S^-$$

in the presence of a proton donor HS. (This implies that electrochemical reduction of superoxide to peroxide is thermodynamically feasible at potentials where V is reduced but that the electrode reaction is very slow.) Peroxide formation in acetonitrile solution has been reported by Lorenzola et al. previously.[8] In that work superoxide was reported to disproportionate in the presence of any available proton donor to form the peroxide species and oxygen. Indeed, the solutions generated here after exhaustive electrolysis in the region of wave I or II were found to contain peroxide ion as evidenced by testing with Fenton's reagent. Thus, if V is continuously regenerated in the presence of oxygen, the diffusion-limited current to the electrode will be expected to increase as observed, without the production of any other product of V.

A plot of the normalized (to the square root of the sweep rate) magnitude of the current as a function of the sweep rate is shown in Figure 3 for the system. The lowest plot (I) is that for the oxygen reduction peak in Figure 1b. The next plot (II) is that for the reduction peak in Figure 1a, the uncomplicated one-electron reduction of V to its anion radical. Plot III is for the second reduction peak in Figure 2, which is the sum of the currents for the reduction of V to its anion radical and the reduction of the electroactive products formed from the anion radical and oxygen, which

---

(6) Siegerman, H. In *Technique of Electroorganic Synthesis, Part II*; Weinberg, N. L., Ed.; Wiley: New York, 1975.

(7) *Encyclopedia of Electrochemistry of the Elements*, Bard, A. J., Lund, H., Eds.; Marcel Dekker: New York, 1978; Volume XI-1.

(8) Lorenzola, T. A.; Lopez, B. A.; Giordano, M. C. *J. Electrochem. Soc.* **1983**, *130*, 1359.

(9) The literature half-wave potential data were taken from ref 6 and 7, assuming where necessary that the potential of the Ag/$Ag^+$ (0.01 M) reference electrode is about 0.3 V more positive than the potential of a saturated calomel electrode in acetonitrile.[6]

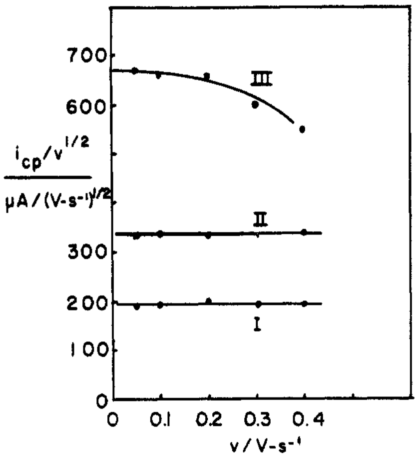


**Figure 3.** Normalized cyclic voltammetric peak current–sweep rate plots of the data in Figures 1 and 2. I is that for the reduction peak in Figure 1b, II is that for the reduction in Figure 1a, and III is for the second reduction peak in Figure 2. Except for the sweep rate, the system parameters are the same as those described in Figure 1.

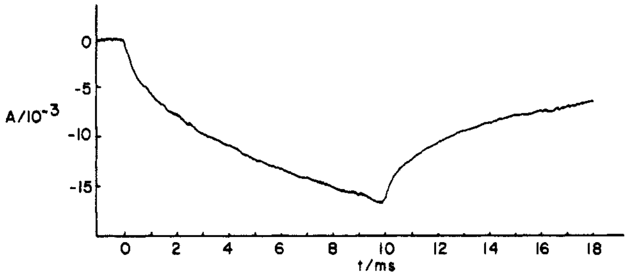


**Figure 4.** Reflectance spectroscopic transient for the absorbance of the anion radical of V in the solution described in Figure 1a. The solution is oxygen free.

is probably more regenerated V as suggested in the previous paragraph.

**Spectroelectrochemistry.** Reflection spectroelectrochemical transients for the formation of the anion radical of V at the platinum mirror electrode in the absence of oxygen are shown in Figure 4. The wavelength of maximum absorption of the anion radical is 519 nm. (A composite spectrum of the anion radical was obtained by plotting absorbance values taken at a given time after the electrochemical step was applied as a function of wavelength. The wavelength of maximum absorption of the anion radical was taken to be that wavelength that gave the maximum absorbance change per unit time.) Composite transient data from 100-, 200-, 400-, and 1000-ms transients were combined to examine the linearity of the optical response with the square root of time over extended periods. Linearity is representative of the stability of the anion radical in the time period examined. The plots were linear with a correlation coefficient $R = 0.99993$; this demonstrates the reproducibility and accuracy of this technique under these conditions and shows the anion radical to be very stable for times up to 1 s. In Figure 5 we have the transient that results at the same wavelength with oxygen present in the system. Superoxide does not absorb at this wavelength. (The modulated specular reflectance spectrum of this mixture still only shows a single absorbance maximum at 519 nm.) The formation of the anion radical is still observed in the forward potential step.

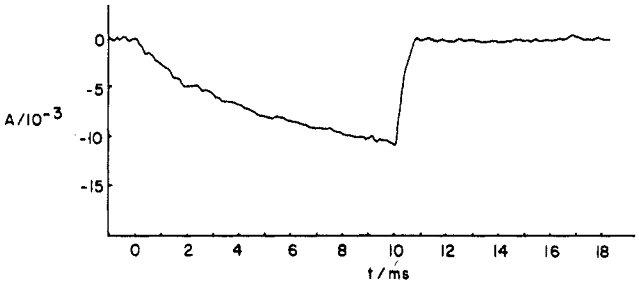


**Figure 5.** Reflectance spectroscopic transient for the absorbance of the anion radical of V in the solution described in Figure 2 (oxygen present).

When the potential is reversed to its starting value (where only V and oxygen are stable), the absorbance is seen to decay rapidly to zero. This is a clear indication that the anion radical of V reacts rapidly with oxygen. The absorbance values in the forward potential step indicate that the starting material V is regenerated in the process, since the shape of the transient is still a linear function of the square root of time. Thus V is formed as $V^{\bullet -}$ diffuses from the electrode into the oxygen and superoxide rich solution.

The results are consistent with and we, therefore, propose the following mechanism for the cathodic reduction of V:

in the absence of oxygen

$$V + e^- \rightleftarrows V^{\bullet -} \qquad E^\circ = -1.93\ \mathrm{V}$$

in the presence of oxygen

$$O_2 + e^- \rightleftarrows O_2^- \qquad E^\circ = -1.18\ \mathrm{V}$$

$$V + e^- \rightleftarrows V^{\bullet -} \qquad E^\circ = -1.93\ \mathrm{V}$$

$$O_2 + V^{\bullet -} \rightleftarrows O_2^- + V$$

$$HS + O_2^- + V^{\bullet -} \rightleftarrows HO_2^- + V + S^-$$

The standard potential for dioxygen reduction has been taken as the mean of the oxidation and reduction peaks. The rapid decay of the anion radical transient is due to the reaction of molecular oxygen with the anion. The rate of production of the anion at the electrode is controlled by the diffusion of the neutral molecule to the interface. As anion reacts with oxygen to regenerate the neutral molecule, more of the neutral molecule is available to diffuse to the interface. In this way the absorbance of the anion is not much lower than it is in the oxygen-free solution. In the reverse pulse experiment however, the oxygen consumes the anion while the electrode can no longer replace it; the absorbance falls rapidly compared to the oxygen-free solution.

Abstraction of the proton by the peroxide dianion most likely occurs from the supporting electrolyte. A study of this point and the general reaction of oxygen and its electrogenerated ions with organic substrates and their ions is under way and will appear elsewhere. Further electrochemical studies on these and related strained systems are also underway and will be the subject of future reports.

**Acknowledgment.** S.P. thanks the Office of Naval Research for support of part of this work. P.J.S. acknowledges the support of the National Science Foundation (CHE84-19099).

**Registry No.** V, 92012-57-2; V anion radical, 101954-73-8.