

Table I. Diffuse Reflectance Infrared and Photoluminescence Spectra of Surface Vanadyl Groups

support	content, wt %	wavenumber ^a of V=O, cm ⁻¹	bond length ^b of V=O, Å		photoluminescence ^c			
					E _X ^{max} , nm	E _M ^{max} , nm	intensity ^c	
none	100	1026	1.571				0	
SiO ₂	1.0	1035	927	1.561	1.685	320	501	0.56
	3.3	1035	927	1.561	1.685	320	504	1.00
	4.2	1035	927	1.561	1.685	320	504	0.50
	7.2	1035	937	1.561	1.673	323	506	0.87
	8.0	1035	943	1.561	1.667	323	511	0.19
	13.6	1032	943	1.564	1.667	323	522	0.19
	29.8	1032	954	1.564	1.654	323	524	0.16
γ-Al ₂ O ₃	5.3	1016		1.583		323	533	0.02
α-Al ₂ O ₃	5.1	1043		1.552		295	523	0.02
MgO	5.1		922		1.691	320	554	0.12
TiO ₂	5.2		912		1.702			0

^a See footnote 1 in the text. ^b See footnote 2 in the text. ^c Relative intensity at 77 K.

The shapes and intensities of the phosphorescence spectra of the supported V₂O₅ samples were strongly dependent on the kinds of supports and the contents, as shown in Figure 1 and Table I.¹⁰ The V₂O₅ and V₂O₅/TiO₂ samples did not show any phosphorescence spectra. This phosphorescence is attributed to the electron-transfer process from T₁(V⁴⁺-O⁻) to S₀(V⁵⁺=O²⁻), resulting in the disappearance of pairs of hole centers (O⁻) and trapped electrons (V⁴⁺).^{11,12} Although the presence of fluorescence has been previously reported on V₂O₅, MoO₃, and WO₃ supported on porous Vycor glass,^{12,13} no fluorescence has been observed in the present study, in conformity with the results on V₂O₅/SiO₂ and MoO₃/SiO₂ by Kazansky et al.¹¹ and Iwasawa et al.¹⁴

As shown in Figure 1, the phosphorescence spectrum from V₂O₅/SiO₂ has a well-resolved vibrational structure. The energy separation of the vibrational bands in the spectrum is in agreement with the surface vanadyl groups. For example, the separation between the 0-0 (440 nm) and 0-1 (461 nm) transitions corresponds to an energy of 1035 cm⁻¹, which was the same as that observed in the IR measurement. It is concluded from the spectra, using the Franck-Condon principle,¹⁵ that the nuclear distance of the V⁵⁺=O²⁻ complex will become longer in the excited states. The intensity of phosphorescence from V₂O₅/SiO₂ showed a volcano-shaped dependence on the degassing temperatures of the sample.¹⁰ The intensity increased steadily from 300 to 573 K. This is ascribed to a decrease of quenching by adsorbed oxygen.^{12,16} On the other hand, the phosphorescence decreased to a certain extent with heightening the evacuation temperatures from 573 to 773 K. Such behavior is due to desorption of oxygen from the V=O bonds.¹²

The present results are helpful in understanding heterogeneous catalysis. For example, one-step hydroxylation of benzene to phenol using N₂O as an oxidant has very recently been reported over V₂O₅-containing catalysts.¹⁷ The promoting effect of carriers on the phenol formation was SiO₂ >> MgO > γ-Al₂O₃ > α-Al₂O₃ ≈ TiO₂. It was also found that 1-10 wt % V₂O₅ content on SiO₂ was effective, the maximum yield of phenol being achieved at 3.3 wt %.¹⁷ It is of significant interest to note that the catalytic activities are roughly proportional to the relative intensities of phosphorescence. This suggests that the vanadyl groups evolving phosphorescence act as active sites for the phenol synthesis or that

O⁻ species in the T₁(V⁴⁺-O⁻) state, which may be formed through the reaction V³⁺ + N₂O → V⁴⁺-O⁻ + N₂ during the catalytic run, is an active oxygen-yielding phenol from benzene. In photocatalysis, Yoshida et al.¹⁸ have found that photocatalytic oxidation of CO proceeds over V₂O₅/SiO₂ but scarcely over V₂O₅/Al₂O₃. Taking into consideration that the T₁(V⁴⁺-O⁻) species is active for this reaction,¹² the results by Yoshida et al. are clarified by the present findings. Similar discussion is possible for the photocatalytic oxidation of propene.¹⁹

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Registry No. SiO₂, 7631-86-9; Al₂O₃, 1344-28-1; TiO₂, 13463-67-7; MgO, 1309-48-4.

(18) Yoshida, Y.; Matsumura, Y.; Noda, S.; Funabiki, T. *J. Chem. Soc., Faraday Trans. 1* 1981, 77, 2237.

(19) Yoshida, Y.; Magatani, Y.; Noda, S.; Funabiki, T. *J. Chem. Soc., Chem. Commun.* 1981, 601.

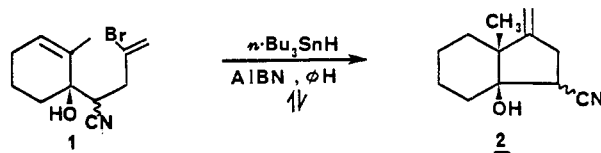
Vinyl Radical Cyclization. 2. Dicyclization via Selective Formation of Unsaturated Vinyl Radicals by Intramolecular Addition to Triple Bonds. Applications to the Synthesis of Butenolides and Furans

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We have recently shown¹ that the cyclization of vinyl radicals is a valuable synthetic method illustrated, inter alia, by the transformation of **1** to **2**.



The compatibility with unprotected functional groups such as the free hydroxyl of **1** and the relative insensitivity to steric hindrance that allows the formation of bonds resulting in quaternary centers will undoubtedly be found to be general features of most radical cyclization processes. Additionally, the vinyl radical cyclization has the chemically valuable feature that the resulting ring has a double bond in a predetermined position.

(1) Stork, G.; Baine, N. H. *J. Am. Chem. Soc.* 1982, 104, 2321.

(10) After being mounted in a quartz cell, the V₂O₅-containing sample was evacuated at 773 K for 2 h, exposed to oxygen (P_{O₂} = 13.3 kPa), and cooled down to ambient temperature in the presence of oxygen. Subsequent to this pretreatment, the sample was degassed at increasing, stepwise, temperatures and subjected to the photoluminescence measurement at 77 K.

(11) Kazansky, V. B. *Proc. 6th. Int. Congr. Catal.* 1977, 50.

(12) Anpo, M.; Tanahashi, I.; Kubokawa, Y. *J. Phys. Chem.* 1980, 84, 3440.

(13) Anpo, M.; Tanahashi, I.; Kubokawa, Y. *J. Phys. Chem.* 1982, 86, 1.

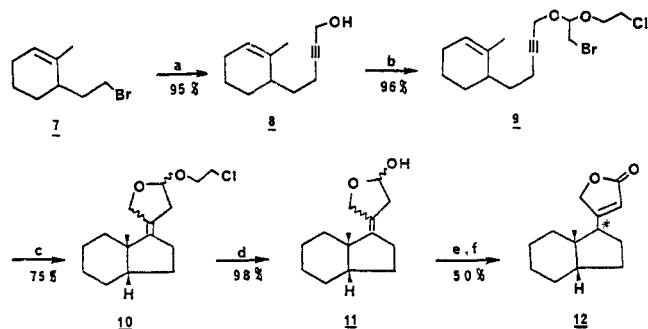
(14) Iwasawa, Y.; Ogasawara, S. *Bull. Chem. Soc. Jpn.* 1980, 53, 3709.

(15) Turro, N. J. "Modern Molecular Photochemistry"; Benjamin/Cummings: Menlo Park, CA, 1978.

(16) Anpo, M.; Yun, C.; Kubokawa, Y. *J. Chem. Soc., Faraday Trans. 1* 1980, 76, 1014.

(17) Iwamoto, M.; Hirata, J.; Matsukami, K.; Kagawa, S. *J. Phys. Chem.* 1983, 87, 903.

Scheme I



^a $\text{LiC}\equiv\text{C}-\text{CH}_2\text{OLi}$ (2 equiv of LiNH_2), NH_3 , -33°C , 4 h.
^b $\text{C}_6\text{H}_5\text{N}(\text{CH}_3)_2$, $\text{BrCH}_2\text{CH}(\text{Br})\text{OCH}_2\text{CH}_2\text{Cl}$, CH_2Cl_2 , room temperature, overnight. ^c 1.1 equiv of Bu_3SnH ; see footnote 6.
^d Sodium, THF/ NH_3 , -78°C . ^e Pyridinium chlorochromate in CH_2Cl_2 . ^f DBU, THF, room temperature, overnight.

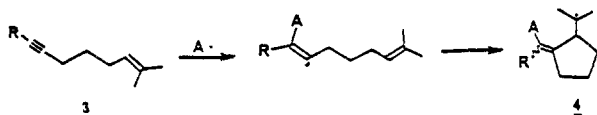
These valuable features led us to seek new methods for the generation of vinyl radicals to supplement the classical reaction of a vinyl halide with a stannane.

The intermolecular addition of a free radical to a triple bond initially appeared an unlikely candidate for the generation of a vinyl radical capable of cycloaddition to a preexisting olefin. The success of this process (cf. 3 \rightarrow 4) would require not only that



the radical entity A be selective for the triple bond but also that it add regioselectively to the latter. Existing data are contrary to these expectations,² at least when A is a carbon-centered radical.

We now show that a simple geometric constraint provides a general solution to both of these regiochemical problems. If the radical center C is connected to the acetylenic link by a chain of three (or possibly four) atoms, cyclization would result in the regioselective formation of the requisite vinyl radical (cf. 5 \rightarrow 6).³



The vinyl radical thus formed can now end the process by hydrogen atom transfer to give the simple cyclized product 6. The process need not stop there, however. The vinyl radical could react with a suitable double bond in the chain R, in the type of cyclization we have studied previously.¹ We illustrate the feasibility and usefulness of this last process by its application to the synthesis of a butenolide attached to a cyclopentane ring. One such sequence is shown in Scheme I, starting with the propargyl alcohol 8.⁴

(2) Kharasch, M. S.; Jerome, J. J.; Urry, W. H. *J. Org. Chem.* **1950**, *15*, 966. Gazith, M.; Szwarc, M. *J. Am. Chem. Soc.* **1957**, *79*, 3339. Abel, P. I. In "Comprehensive Chemical Kinetics"; Bamford, C. H., Tripper, C. F. H., Eds.; Elsevier: Amsterdam, 1976; Vol. 18. Giese, B.; Lachhein, S. *Angew. Chem.* **1982**, *94*, 780.

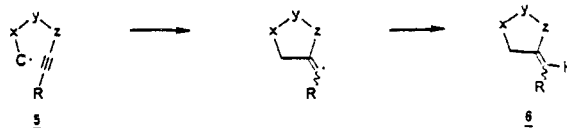
(3) For a recent example of an intramolecular addition of a carbon-centered radical to a triple bond, see: Hart, D. J.; Choi, J.-K.; Tsai, Y.-M. *Tetrahedron Lett.* **1982**, *23*, 4765.

(4) Bromide 7 was made by the ortho ester Claisen rearrangement of 2-methyl-2-cyclohexenol followed by hydride reduction, tosylate formation, and displacement with lithium bromide.

(5) Prepared (bp $70-75^\circ\text{C}$ (0.25 mm Hg)) by addition of bromine to commercially available (Polysciences) 2-chloroethyl vinyl ether.

(6) All cyclizations were performed essentially in the same manner in benzene under argon with 1.1 equiv of Bu_3SnH (0.02 M) and 0.05 equiv of AIBN as initiator. After 3-8 h of refluxing, workup was with potassium fluoride as described: Jacobs, J.; Leibner, J. E. *J. Org. Chem.* **1979**, *44*, 449.

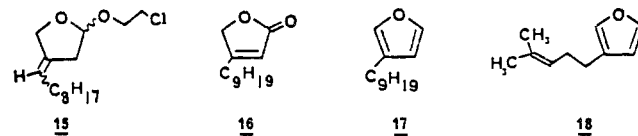
The structure and stereochemistry of the product of double cyclization were^{8,9} confirmed by ozonolysis to the known *cis*-methylhydrindanone¹⁰ 13 and the furanone 14 (63% and 77%



yield, respectively). The former had the characteristic IR absorption at 1740 cm^{-1} and methyl singlet at δ 1.06 in the NMR. The furanone had an IR absorption at 1760 cm^{-1} and the following: NMR δ 5.56 (H_a , d, 6 Hz), 2.69 (H_c , dd, $J = 6, 16$ Hz), 2.47 (H_b , d, $J = 6$ Hz).

The chloroethyl protecting group was used because of the sensitivity of the system in 10 to the required acid hydrolysis conditions. Removal of the chloroethyl group with sodium in THF-ammonia proved extremely efficient. The final unsaturated lactone 12 had the following IR $1790-1740\text{ cm}^{-1}$; NMR δ 5.9 (1 H, d, $J = 2$ Hz), 4.8 (2 H, dd, $J = 2, 12$ Hz), 1.02 (3 H, s).¹¹

The initial radical addition to a triple bond is, of course, valuable even when it simply terminates at the vinyl radical stage because that process, like the vinyl cyclization, places double bonds in a specific position. For example, the bromoacetal from 2-undecynol leads as above (70% yield) to the cyclic acetal 15.^{12,13} The sequence shown in 10-12 readily transforms such acetals to the corresponding β -substituted butenolides (cf. 16).



The same cyclic acetal 15 also allows a simple synthesis of β -substituted furans, a system that occurs in a number of natural products. Thus, transformation of 15 to a furan is readily accomplished by treatment of a benzene solution of 15 (0.07 M, pTSA catalyst, 4-Å molecular sieves, 2 h reflux) to give 3-nonylfuran (17) in 70% yield (NMR δ 7.38 (1 H, d, $J = 1-2$ Hz), 7.22 (1 H, d, $J = 1-2$ Hz), 6.30 (1 H, d, $J = 1-2$ Hz), 2.42 (2 H, t, $J = 7$ Hz). The naturally occurring β -substituted furan perillene¹⁴ (18) was made by the same sequence, starting with the appropriate propargyl alcohol.¹⁵

(7) Anhydrous ammonia is added to the THF suspension until the sodium breaks up into very small beads.

(8) Reaction products were examined by capillary GLC, NMR, and IR spectroscopy and, in the case of 12, by mass spectrometry (M^+ 284.286). Cyclizations were run under an argon atmosphere. Purification was by flash chromatography (Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923).

(9) The unsaturated cyclic acetal 10 (cf. 7) is a mixture of *E* and *Z* isomers (because of the very low inversion barrier of the vinyl radical precursor). This ambiguity disappears, of course, in the transformation to the butenolides (e.g., 12) or furans.

(10) Lansbury, P. T.; Briggs, P. C.; Demmin, T. R.; DuBois, G. E. *J. Am. Chem. Soc.* **1971**, *93*, 1311.

(11) The stereochemistry at the starred center in 12, which appears to be a single substance, was not determined. The infrared spectrum of 12 shows a broad carbonyl absorption typical of α -unsubstituted α,β -unsaturated lactones.

(12) The beneficial effect of β -alkoxy groups in radical cyclization reactions into a double bond has been noted: Beckwith, A. L. J.; Blair, I.; Philipou, G. *J. Am. Chem. Soc.* **1974**, *96*, 1613.

(13) For other recent work involving monocyclization of radicals derived from α -bromoacetals and olefins or acetylenes see: Ueno, Y.; Chino, K.; Watanabe, M.; Moriya, O.; Okawara, M. *J. Am. Chem. Soc.* **1982**, *104*, 5564. Okabe, M.; Tada, M. *J. Org. Chem.* **1982**, *47*, 5382. Our work involving cycloaddition of radicals with a β -acetal function, into olefinic as well as acetylenic systems was first reported in Mar 1982, on the occasion of the Edgar Fahs Smith lecture in Philadelphia. It was presented also at the Fourth International Conference on Organic Synthesis, Tokyo, Aug 1982. Cf. Nozaki, H., Ed. "Current Trends in Organic Synthesis"; Pergamon Press: New York, 1983; pp 359 ff.

(14) For other recent routes to β -substituted furans, see (a) Tanis, S. P. *Tetrahedron Lett.* **1982**, *23*, 3115. (b) McMurry, J. E.; Donovan, S. F. *Ibid.* **1977**, 2869.

Acknowledgment. We thank the National Institutes of Health and the National Science Foundation for their support of this work.

Registry No. 7, 85613-84-9; 8, 85613-85-0; 9, 85613-86-1; 10, 85613-87-2; 11, 85613-88-3; 12, 85613-89-4; 13, 13025-91-7; 14, 85613-90-7; 15, 85613-91-8; 17, 40015-00-7; BrCH₂CH(Br)OCH₂C-H₂Cl, 14689-94-2; LiC≡CCH₂OLi, 60851-89-0; 2-(chloroethyl) 2-undecyn-1-yl 2-bromoacetaldehyde acetal, 85613-92-9.

(15) These monocyclizations were also conveniently performed by using a polystyrene-supported tributyltin hydride first prepared in this laboratory by Gary Tennyson, following essentially the route described for the related dihydride (Weinshenker, N. M.; Crosby, G. A.; Wong, J. Y. *J. Org. Chem.* 1975, 40, 1966).

Design, Preparation, and ESR Detection of a Ground-State Nonet Hydrocarbon as a Model for One-Dimensional Organic Ferromagnets

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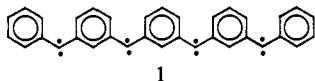
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We have succeeded in detecting by electron spin resonance spectroscopy an aromatic hydrocarbon, *m*-phenylenebis((diphenylmethylene-3-yl)methylene) (**1**), which has eight parallel



spins, i.e., nonet spin multiplicity ($S = 4$) in the electronic ground state. This is the highest spin multiplicity observed in organic as well as inorganic compounds. The prototype of this molecule, *m*-phenylenebis(phenylmethylene) in the quintet ground state ($S = 2$) was found in 1967 independently by one of us¹ and by Wasserman et al.² Some more examples were added to this class of high-spin multiplet hydrocarbons: *m*-phenylenebis(methylene) ($S = 2$),² benzene-1,3,5-tris(phenylmethylene) ($S = 3$),³ 1,3,5-benzenetriyltris(bis(biphenyl-4-yl)methyl) ($S = 3/2$),⁴ and biphenyl-3,3'-bis(phenylmethylene) ($S = 0, 1, \text{ and } 2$).⁵

The molecule **1** is an even alternant hydrocarbon. We assume that one of the unpaired electrons of each divalent carbon atom participates in conjugation with the π system of the benzene rings while the other remains in the nonbonding orbital "n" localized on the divalent carbon atom. The simple molecular orbital theory⁶ predicts that the π system has four singly occupied nonbonding MO's, which may be nearly degenerate with the four n orbitals. The meta substitution in **1** is essential for the 4-fold degeneracy of the π MO's, which is dictated by the topological symmetry.⁵ Thus, eight parallel spins occupy the eight nearly degenerate orbitals because of Hund's rule as confirmed by the experiment described below. The parallel spins in the π orbitals are delocalized over the whole molecule and are exchange-coupled strongly to the localized spins on the divalent carbon atoms. This interaction resembles closely the one between conducting s electrons and localized d electrons in ferromagnetic transition metals. Therefore, if we consider a long-chain constituted of the unit in **1**, one-dimensional organic ferromagnets may be expected. The possible electronic structure of such polymers was previously discussed by Mataga.⁷ The one-dimensional magnetic systems have been a topic in current physics.⁸

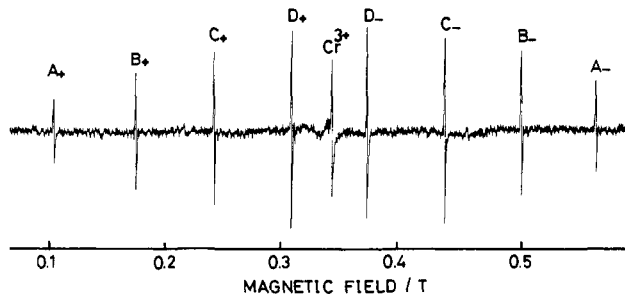
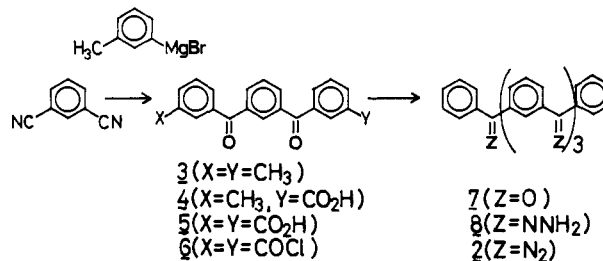


Figure 1. Electron spin resonance spectrum observed after the photolysis at 4.2 K with the magnetic field along the direction 26° from the *a* axis in the *ab* plane of the host crystal. The microwave frequency is 9550.6 MHz. The central line is due to Cr³⁺ in MgO powder used as a reference substance.

Scheme I



1 was generated by UV irradiation of the corresponding diazo compound **2**, which in turn was prepared as shown in Scheme I. Isophthalonitrile was allowed to react with *m*-tolylmagnesium bromide, and the mixture was hydrolyzed with HCl to give di-ketone **3**, mp 101–102 °C, in 80% yield. Heating of **3** under reflux with Na₂Cr₂O₇ in acetic acid produced in quantitative yield monocarboxylic acid **4**, mp 321–326 °C, which then gave dicarboxylic acid **5**, mp 328–334 °C, in 80% yield with KMnO₄ in aqueous alkaline conditions. Treatment of **5** with thionyl chloride gave dichloride **6** as an oil, which was reacted with anhydrous AlCl₃ in benzene to give tetraketone **7**, mp 219.0–219.5 °C, in 78% yield. Tetrahydrazone **8**, mp 105–113 °C, was obtained in 79% yield by the reaction of **7** with hydrazine hydrate in boiling ethanol. Treatment of **8** with active MnO₂ in anhydrous ether in the absence of light and air gave **2**, mp 113 °C dec: IR 2040 cm⁻¹; UV 290 nm (91 600), 522 (416).⁹

The diazo precursor **2** was oriented in single crystals of benzophenone, the concentration being 0.05 mol %. Figure 1 shows the ESR spectrum observed at 4.2 K after photolysis by the 405-nm mercury line.¹⁰ The eight observed lines were found to be the fine structure due to the following $\Delta M_S = \pm 1$ allowed transitions: $A_{\pm} (M_S = \pm 4 \leftrightarrow \pm 3)$, $B_{\pm} (M_S = \pm 3 \leftrightarrow \pm 2)$, $C_{\pm} (M_S = \pm 2 \leftrightarrow \pm 1)$, and $D_{\pm} (M_S = \pm 1 \leftrightarrow 0)$. The relative separations are nearly $(A_- - A_+) : (B_- - B_+) : (C_- - C_+) : (D_- - D_+) = 7.5:3:1$, and the relative integrated intensities are nearly $A_{\pm} : B_{\pm} : C_{\pm} : D_{\pm} = 4:7:9:10$ as expected of $S = 4$ in the high-field approximation. The magnetic field is approximately parallel to the *Z* principal axis of the fine-structure tensor, the deviation being 9.8°, which gives the largest fine-structure splittings.

The angular dependence of the resonance fields and of the signal intensities of the eight lines is well reproduced by the spin Hamiltonian

$$\mathcal{H} = g\beta H \cdot S + D[S_z^2 - \frac{1}{3}S(S+1)] + E(S_x^2 - S_y^2)$$

where $S = 4$, $g = 2.003$, $D = +0.0332 \text{ cm}^{-1}$, and $E = -0.0031 \text{ cm}^{-1}$. Higher terms in *S* group theoretically allowed for $S = 4$ are negligibly small. This fact and the nearly isotropic *g* value

(1) Itoh, K. *Chem. Phys. Lett.* 1967, 1, 235.

(2) Wasserman, E.; Murray, R. W.; Yager, W. A.; Trozzolo, A. M.; Smolinsky, G. *J. Am. Chem. Soc.* 1967, 89, 5076.

(3) Takui, T.; Itoh, K. *Chem. Phys. Lett.* 1973, 19, 120.

(4) Brickman, J.; Kothe, G. *J. Chem. Phys.* 1973, 59, 2807.

(5) Itoh, K. *Pure Appl. Chem.* 1978, 50, 1251.

(6) Longuet-Higgins, H. C. *J. Chem. Phys.* 1950, 18, 265.

(7) Mataga, N. *Theor. Chim. Acta* 1968, 10, 372.

(8) Steiner, M.; Villain, J.; Windsor, C. G. *Adv. Phys.* 1976, 25, 87.

(9) Satisfactory elemental analyses and ¹H and ¹³C NMR spectra were obtained for all new compounds.

(10) A JEOL 3BX ESR spectrometer equipped with a home-made cavity (TE₁₀₂, Q = 6000) and an OSRAM high-pressure mercury lamp (500 W) was used.