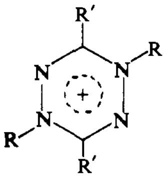
An Electron Spin Resonance Study of Several 1,4-Dihydro-*s*-tetrazine Cation Radicals

W. M. Tolles,[1a] William R. McBride,[1b] and Wayne E. Thun[1b]

Contribution from the Department of Chemistry at the Naval Postgraduate School, Monterey, California 93940, and the Research Department, Naval Weapons Center, China Lake, California 93555. *Received September 30, 1968*

Abstract: The one-electron oxidation of 1,4-dihydro-*s*-tetrazines using concentrated iodine solutions of tetrahydrofuran as oxidant gives rise to a new class of relatively stable cation radicals. In the presence of water and air these radical cations in solution are stable for periods of hours to several days. The esr spectra for radical cations of 1,4-dimethyl-, 1,4-diphenyl-, 1,4-dimethyl-3,6-diphenyl-, 1,3,4,6-tetraphenyl-, and 1,4-bis(*p*-bromophenyl)-3,6-diphenyl-1,4-dihydro-*s*-tetrazines are interpreted and compared with molecular orbital calculations using the CNDO/2 method to obtain the molecular orbital parameters. Assignment of the esr nitrogen coupling constants indicates nearly the same value for the five members of the series studied. The formation of the previously unreported 1,4-dimethyl-1,4-dihydro-*s*-tetrazine, first identified as its radical cation in several different reactions, is discussed.

During an investigation involving the chemistry of 1,1-dialkylhydrazines and 1,1,4,4-tetraalkyl-2-tetrazenes, a long-lived paramagnetic species was observed from the oxidation of 1,1-dimethylhydrazine with excess iodine in neutral solution or an iodine-forming oxidant such as potassium iodate in aqueous sulfuric acid. This paramagnetic species could not be attributed to either the parent dimethylhydrazine or the expected tetramethyl-2-tetrazene. Subsequently, the esr spectrum was unequivocally identified as the cation radical of 1,4-dimethyl-1,4-dihydro-*s*-tetrazine. It is the purpose of the present paper to report the existence of a new class of relatively stable radical cations formed by the one-electron oxidation of 1,4-dihydro-*s*-tetrazines and to interpret the esr spectra of several members of the series. The radical cation in this class of compounds (**1**) is related to two classes of stable neutral free radicals,[2] the verdazyls (**2**) and the tetrazolinyl radicals (**3**), as well as several *s*-tetrazine radical anions[3] (**4**). All of these radical species have seven π electrons and a very small spin density on the ring carbon atoms. In the examples of **2**, **3**, and **4** this small spin density is due to the location of a node at these positions, dictated by symmetry. For **1** the fact that a node is almost located on this carbon atom is accidental.



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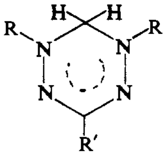

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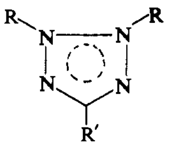

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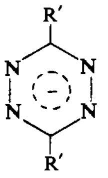

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Experimental Section

Esr spectra were taken with a Varian V-4500 X-band esr spectrometer utilizing 100-KHz modulation. Precise mass values were obtained on a Hitachi Perkin-Elmer double-focusing RMU-6E mass spectrometer. Ultraviolet spectra were measured with a Cary Model 11MS recording spectrophotometer. Nmr spectra were taken with a Varian A-60 spectrometer.

1,4-Dihydro-*s*-tetrazine radical cations are readily observed by the addition of the neutral dihydro-*s*-tetrazine to a concentrated solution of iodine in tetrahydrofuran. An iodine concentration greater than approximately 0.2 *M* is necessary for the observation of a paramagnetic species. Improved resolution is obtained by purging the system with nitrogen gas. Solvents such as acetone or acetonitrile may also be used, but the esr hyperfine patterns are not as well resolved in these solvents. Tetranitromethane can also be used as the oxidizing agent, but the lifetime of the radical cations is on the order of seconds to minutes under these conditions. Interpretation of the esr spectra is confirmed in each case by comparison with computer-simulated plots.

1,4-Dimethyl-1,4-dihydro-*s*-tetrazine was isolated from several different reaction mixtures; method A is the only procedure which gave a substantial yield.

A. Formaldehyde (14.4 ml, 37%) is added dropwise with continuous stirring to 10 ml of methylhydrazine at room temperature over a 0.5-hr period. After 2 hr, solid sodium hydroxide is added to the reaction mixture, whereupon crystals of 1,4-dimethylhexahydro-*s*-tetrazine precipitate from solution. The mixture, after several minutes, is extracted with several fractions of ether (about 300 ml total). Yellow mercuric oxide (35 g) is then added to the stirred ether solution. Initially, the solution turns deep violet with evolution of some gas; after stirring for 17 hr, the solution is yellow. The solvent is removed in a rotary evaporator, leaving a yellow oil which is distilled at 5 torr. The fraction collected between 55 and 59° gives 1.5 g of 1,4-dimethyl-1,4-dihydro-*s*-tetrazine (14% yield). Further purification is effected by vapor phase chromatography through a 0.25-in. column 10 ft in length containing 20% by weight fluorosilicone oil (SF-1265) on Chromosorb W at 135°. The pure light yellow solid, mp 44–46°, is identified by mass spectral analysis of the parent peak: *m*/*e* 112.0749; calcd 112.0743; nmr ($CDCl_3$) τ 3.60 (s, 2 H), 6.97 (s, 6 H); uv max (absolute C_2H_5OH) 237 nm (ε 7900).

B. 1,1-Dimethylhydrazine (2 ml) at room temperature is added slowly to a stirred solution of 100 ml of 1 *M* sulfuric acid containing 5.6 g of potassium iodate. After 10–15 min, approximately 1 ml of a second liquid phase containing mainly iodine forms and settles to the bottom. The esr spectrum of this iodine-rich phase displays an intense but poorly resolved absorption of the 1,4-dimethyl-1,4-dihydro-*s*-tetrazine radical cation with a half-life of approximately 1 week at room temperature. Elimination of iodine from this phase to obtain a tractable sample is accomplished by the dropwise addition of the iodine phase to 20 ml of stirred tetrahydrofuran containing 1–2 g of 325-mesh powdered magnesium, with subsequent centrifuging to remove the magnesium iodide formed. The

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[1] (a) Naval Postgraduate School; (b) Naval Weapons Center.

[2] (a) R. Kuhn, F. A. Neugebauer, and H. Trischmann, *Monatsch. Chem.*, **98**, 726 (1967), and references therein; (b) F. A. Neugebauer and G. A. Russell, *J. Org. Chem.*, **33**, 2744 (1968) (included at the suggestion of a referee).

[3] (a) E. W. Stone and A. H. Maki, *J. Chem. Phys.*, **39**, 1635 (1963); (b) E. T. Strom, G. A. Russell, and R. Konaka, *ibid.*, **42**, 2033 (1965); (c) G. A. Russell, R. Konaka, E. T. Strom, W. C. Danen, K. Chang, and G. Kaupp, *J. Amer. Chem. Soc.*, **90**, 4646 (1968).

1,4-dimethyl-1,4-dihydro-*s*-tetrazine exists as the neutral species at this point. The sample which is distilled at room temperature (0.001 torr) and passed through a vapor chromatographic column reveals at least ten different materials. One of the minor products is characterized as the radical cation of 1,4-dimethyl-1,4-dihydro-*s*-tetrazine by its esr spectrum after addition to iodine in tetrahydrofuran.

C. 1-Formyl-1-methylhydrazine is prepared initially from methylhydrazine and ethyl formate according to the method of Pederson.[4] The 1-formyl-1-methylhydrazine after several hours is added to an iodine solution in tetrahydrofuran. The solution exhibits the esr spectrum of the 1,4-dimethyl-1,4-dihydro-*s*-tetrazine cation radical. Vapor chromatographic separation reveals a small amount (about 0.1% yield) of 1,4-dimethyl-1,4-dihydro-*s*-tetrazine.

1,4-Dimethylhexahydro-*s*-tetrazine was prepared using the procedure in method A for the preparation of 1,4-dimethyl-1,4-dihydro-*s*-tetrazine. Prior to the addition of mercuric oxide the ether solution was evaporated to dryness in a rotary evaporator. The solid material thus obtained was recrystallized from *n*-hexane and further purified by fractional sublimation under a vacuum of 0.5–1.0 torr. This material is the higher melting dimer of formaldehyde methylhydrazone reported by Müller and Rundel[5] and referred to by Elderfield[6] and Schmitz and Ohme[7] as being the hexahydro-*s*-tetrazine: mp 122–124°; *m/e* 116.1033; calcd 116.1062; nmr ($CDCl_3$) τ 6.40 (s, 4 H), 7.1 (s, 2 H), 7.62 (s, 6 H). The CH_2 and NH peaks are broad at room temperature, but narrow at 65°. At low temperatures they break into an ABC multiplet. (Behavior such as this has been reported recently for 1,2,4,5-tetramethylhexahydro-*s*-tetrazine by Anderson and Roberts.[8])

In an attempt to prepare this material according to the method of Hunt and Hough[9] from methylhydrazine and methylene chloride in ether, we were unable to isolate the crystalline material from the reaction mixture as described in the reference. An X-ray crystal powder pattern of the 1,4-dimethylhexahydro-*s*-tetrazine isolated by the procedure in the preceding paragraph did not agree with the powder pattern presented in this patent.

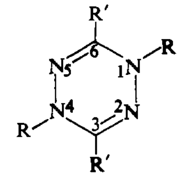
1,4-Dimethyl-1,2,3,4-tetrahydro-*s*-tetrazine was obtained from the preparation of 1,4-dimethyl-1,4-dihydro-*s*-tetrazine (method A) by collecting 0.8 ml of the distillate from 60 to 100° (5 torr). This fraction was purified by vapor phase chromatography in a manner similar to that used for 1,4-dimethyl-1,4-dihydro-*s*-tetrazine. The material is a colorless liquid at room temperature: *m/e* 114.0925; calcd 114.0905; nmr ($CDCl_3$) τ 3.20 (s, 1 H), 5.50 (s, 1 H, broad), 6.52 (d, 2 H, $J = 8.5$ Hz), 7.16 (s, 3 H), 7.35 (s, 3 H); uv max (absolute C_2H_5OH) 242 nm (ε 5700).

1,3,4,6-Tetraphenyl-1,4-dihydro-*s*-tetrazine was prepared according to the method of Bamberger and Grob[10] by oxidation of the phenylhydrazone of benzaldehyde with iodine in basic media. Separation of the product was not achieved by fractional crystallization in the final stages of the preparation. This difficulty has been mentioned elsewhere.[11] Purification of the *s*-tetrazine from the brown-red crystals was accomplished using dry column chromatography[12] over 200-mesh silica gel with a 50 : 50 *n*-hexane–benzene solvent. Approximately 500 mg of the *s*-tetrazine was isolated by this technique: mp 204–205.5°; uv max (absolute C_2H_5OH) 271 nm (ε 17,900) and 332 (13,000).

Anal. Calcd for $C_{26}H_{20}N_4$: C, 80.37; H, 5.19; N, 14.43. Found: C, 80.46; H, 5.22; N, 13.83.

1,4-Bis(*p*-bromophenyl)-3,6-diphenyl-1,4-dihydro-*s*-tetrazine was prepared by oxidizing benzaldehyde phenylhydrazone with bromine in acetic acid.[13] The *s*-tetrazine was recrystallized from acetic acid as yellow crystals: mp 264° (lit.[13] mp 265°); uv max (absolute C_2H_5OH) 275 nm (ε 19,100) and 337 (18,600).

Table I. Esr Coupling Constants of Some 1,4-Dihydro-*s*-tetrazine Radical Cations at Room Temperature Produced by Addition of the *s*-Tetrazine to Iodine in Tetrahydrofuran



R	R′		Coupling constant, G Exptl	Calcd
CH_3	H	a_1(N)	7.95 ± 0.05	7.33
		a_2(N)	4.40 ± 0.05	4.60
		$a(CH_3)$	8.33 ± 0.05	6.95
		a_3(CH)	<0.2	0.80
		Line width	0.2	
C_6H_5	H	a_1(N)	7.36 ± 0.02	5.10
		a_2(N)	3.39 ± 0.02	3.62
		a^a(H)	1.51 ± 0.02	1.15[b]
		a_3(CH)	0.60 ± 0.02	0.65
		Line width	0.16	
CH_3	C_6H_5	a_1(N)	7.80 ± 0.2	6.80
		a_2(N)	4.51 ± 0.02	4.29
		$a(CH_3)$	7.80 ± 0.2	6.45
		Line width	0.4	
C_6H_5	C_6H_5	a_1(N)	7.4 ± 0.2	6.05
		a_2(N)	4.3 ± 0.2	4.10
		a^a(H)	0.48 ± 0.02	See
		Line width	0.3	Figure 2
p-Br-C_6H_4	C_6H_5	a_1(N)	7.4 ± 0.2	
		a_2(N)	4.3 ± 0.2	
		a(H)	0.50 ± 0.04	
		Line width	0.4	

[a] Molecular orbital calculations indicate that the *ortho* and *para* coupling constants of C_6H_5 on the nitrogen atom are equal (within 2%) and that all other benzene ring coupling constants are negligible. [b] Assuming coplanarity between ring systems.

Anal. Calcd for $C_{26}H_{18}N_4Br_2$: C, 57.15; H, 3.32; N, 10.26; Br, 29.27. Found: C, 57.08; H, 3.28; N, 10.21; Br, 29.43.

1,4-Diphenyl-1,4-dihydro-*s*-tetrazine was obtained by silver oxide oxidation of 1,4-diphenylhexahydro-*s*-tetrazine which was prepared by the reaction of formaldehyde with phenylhydrazine.[14] The light yellow platelets were recrystallized from toluene: mp 194–195° (lit.[14] mp 193–194°); uv max (absolute C_2H_5OH) 295 nm (ε 27,000). The spectrum for this compound has been reported.[15]

Anal. Calcd for $C_{14}H_{12}N_4$: C, 71.16; H, 5.12; N, 23.72. Found: C, 70.99; H, 5.06; N, 23.75.

1,4-Dimethyl-3,6-diphenyl-1,4-dihydro-*s*-tetrazine cation radical was observed by two procedures. Iodine in tetrahydrofuran was added to the reaction mixture obtained from the basic oxidation of benzaldehyde methylhydrazone, following a procedure analogous to that for the 1,3,4,6-tetraphenyl-1,4-dihydro-*s*-tetrazine. An esr multiplet pattern was observed which readily indicated the presence of the desired *s*-tetrazine cation. Thin layer chromatography of the reaction mixture revealed numerous products, making separation by dry column chromatography nearly impossible. A second method for the observation of this radical cation was to follow the procedure analogous to the preparation of 1,4-dimethyl-1,4-dihydro-*s*-tetrazine, using mercuric oxide as an oxidizing agent. Addition of this reaction mixture to iodine in tetrahydrofuran gave a pattern identical with that obtained by the previous method. Isolation of the *s*-tetrazine from this reaction mixture again proved difficult. Since it is felt that isolation of the neutral dihydro-*s*-tetrazine would not improve the spectral resolution significantly, characterization of the previous examples is believed sufficient for the identification of the esr spectrum.

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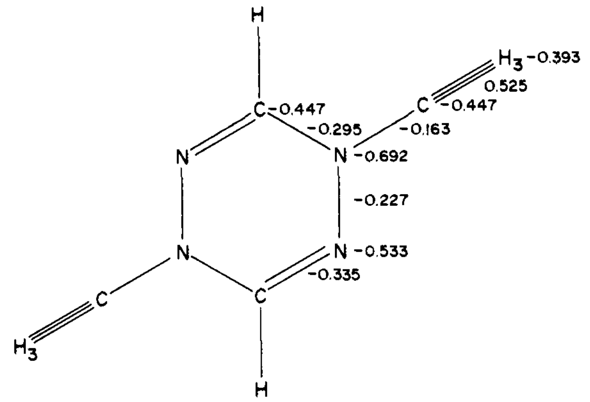

Figure 1. Molecular orbital parameters for 1,4-dimethyl-1,4-dihydro-*s*-tetrazine obtained by using the CNDO/2 method. The number adjacent to an atom represents the self-consistent coulomb integral for that atom, and that adjacent to a bond represents the resonance integral between the two atoms.

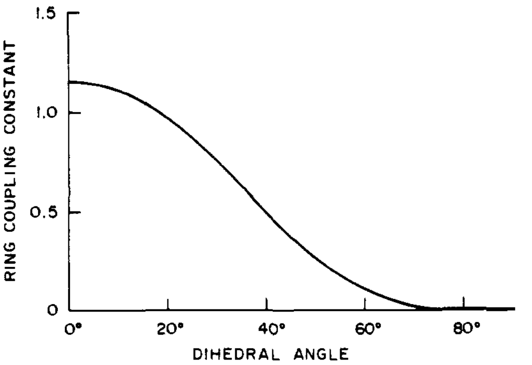

Figure 2. Calculated coupling constants for the *ortho* and *para* positions of a benzene ring substituted on the 1,4 positions of a dihydro-*s*-tetrazine cation as a function of the dihedral angle between the *s*-tetrazine and benzene ring.

Results and Discussion

All of the 1,4-dihydro-*s*-tetrazines studied, when placed in concentrated iodine solutions of tetrahydrofuran and examined by esr, demonstrated the existence of paramagnetic species. The experimental coupling constants obtained from an assignment of the esr spectra are presented in Table I, together with calculated coupling constants.

The assignment of the larger and smaller nitrogen coupling constants, corresponding to the 1,4 and 2,5 positions, respectively, is unambiguous due to the approximate relationship involving the hydrogen–nitrogen coupling constant ratio for an N–CH_3 group.[16] The assignment of coupling constants to other positions is made on the basis of molecular orbital calculations. The spectra of the two tetraaryl-*s*-tetrazine radical cations are not well resolved, but assignment of the 0.5-G coupling constant to the *ortho* and *para* positions of the aryl group in the 1,4 positions is strongly indicated by calculations.

A generally accepted set of molecular orbital parameters for the carbon and nitrogen atoms represented herein is not available; thus the approximate SCF CNDO/2 method of Pople and Segal[17] was used to calculate spin densities of the 1,4-dimethyl-1,4-dihydro-*s*-tetrazine radical cation. The computer program was written in this laboratory, the input consisting of atomic numbers, bond lengths, and bond angles. The coordinates are generated by rotation and translation of the coordinate system. Agreement of the calculations with experiment is excellent considering that no adjustable parameters were introduced beyond those of the original CNDO/2 method.

Molecular orbital calculations on other members of the series were performed with the aid of the SCF matrix elements for the π orbitals obtained from the CNDO/2 calculation of 1,4-dimethyl-1,4-dihydro-*s*-tetrazine cation. These parameters are given in Figure 1. Matrix elements between nonnearest neighbors were neglected without seriously affecting the distribution of the unpaired electron. The molecular orbital parameters for the methyl group were obtained by transforming the hydrogen atom basis to a representation in which the σ and π orbitals did not interact. The carbon coulomb integral in Figure 1 was used throughout the calculations of the substituted *s*-tetrazine cations. The C–C resonance integral was approximated to be -0.300 by comparison with calculations on this and other molecules.

The calculated nitrogen coupling constants were obtained assuming the relation $a^N = Q^N{}_N\rho^N$, which introduces only a small error as compared to the corresponding expression involving spin densities on atoms adjacent to nitrogen.[3a] The $Q^N{}_N$ value of 26.8 is obtained by using this same expression with the reported coupling constants for the tetramethylhydrazine cation.[18] Other values used were $Q^H{}_{NCH_3} = 25.4$ and $Q^H{}_{CH} = 24.0$.

The coupling constants for the *s*-tetrazine ring remain nearly unchanged as the substituents in the 1, 3, 4, and 6 positions are varied. In the case of the 1,4-diphenyl-1,4-dihydro-*s*-tetrazine cation appreciable delocalization of the unpaired electron into the nearly coplanar benzene rings accounts for a slight decrease in the nitrogen coupling constants. The nitrogen coupling constants of the 1,3,4,6-tetraphenyl-1,4-dihydro-*s*-tetrazine cation are similar to those of 1,4-dimethyl-1,4-dihydro-*s*-tetrazine cation, indicating less conjugation of the neighboring ring systems due to steric interaction. The noncoplanarity of the 1,3,4,6-tetraphenyl-1,4-dihydro-*s*-tetrazine cation is also indicated by the smaller *ortho* and *para* coupling constants observed for this species. Coupling constants in the *ortho* and *para* positions of a 1-substituted benzene ring are calculated in Figure 2 for various angles of twist between the *s*-tetrazine and benzene rings, assuming a $\cos^2\theta$ dependence of the N–C resonance integral. The observed splitting in the 1,3,4,6-tetraphenyl-1,4-dihydro-*s*-tetrazine cation indicates the angle between the benzene and *s*-tetrazine rings is approximately 40°.

Although detailed mechanisms for the formation of these 1,4-dihydro-*s*-tetrazines are not completely understood at this time, certain comments concerning their preparation seem appropriate. Tetraaryl-substituted 1,4-dihydro-*s*-tetrazines were prepared by several different routes, presumably with dipolar nitrilimines as intermediates in many of the reactions.[6] Huisgen and coworkers[15] obtained evidence that electron-attracting sub-

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stituents on both the carbon and nitrogen atoms of the nitrilimine promote the formation of 1,4-dihydro-*s*-tetrazines; experimentally, several reaction paths were observed in the formation of the *s*-tetrazines.

1,4-Dihydro-*s*-tetrazines with more weakly electron-attracting or electron-repelling substituents, such as alkyl-substituted derivatives, are better prepared by oxidation of the corresponding hexahydro-*s*-tetrazines. The reaction of formaldehyde with aryl-[14] or alkyl-monosubstituted[5,7] hydrazines gives a variety of products. Since the simple hydrazone is often not capable of stable existence,[19,20] the dimer or a hexahydro-*s*-tetrazine can be a major product of the reaction. Skorianetz and Kovats[21] describe high concentration, low temperature, and basic medium as conditions conducive to the formation and stabilization of aliphatic hexahydro-*s*-tetrazines. Selective oxidation of the hexahydro-*s*-tetrazine with mercuric oxide gives both the 1,2,3,4-tetrahydro-*s*-tetrazine and the 1,4-dihydro-*s*-tetrazine. 1,4-Dimethyl-1,4-dihydro-*s*-tetrazine cation radical was identified from oxidation reactions of 1,1-dimethylhydrazine, 1,2-dimethylhydrazine, 1-formyl-1-methylhydrazine, methylhydrazine, and equimolar mixtures of methylhydrazine–formaldehyde. The several reactions, some with very poor yields, undoubtedly have a commonality in their condensation to the *s*-tetrazine, regardless of the oxidation state of the labile monomer. Formally, formaldehyde and methylhydrazine may be considered as the most likely reactants. Iodate ion in aqueous solution, like mercuric sulfate,[22] oxidizes one methyl group of 1,1-dimethylhydrazine to formaldehyde. 1-Formyl-1-methylhydrazine may hydrolyze to formaldehyde and methylhydrazine in a manner similar to that observed for substituted formamides.[23] 1,2-Dimethylhydrazine is oxidized to azomethane which may isomerize[24] to formaldehyde methylhydrazone.[25]

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Double-Bond Fixation in Conjugated π-Electron Systems. IV. Self-Consistent Field Formalism and Applications to Alternant Hydrocarbons

Gerhard Binsch,[1a] Ilana Tamir, and R. Dean Hill[1b]

Contribution from the Department of Chemistry and the Radiation Laboratory,[2] University of Notre Dame, Notre Dame, Indiana 46556. *Received October 14, 1968*

Abstract: The theory of double-bond fixation in conjugated π-electron systems, developed in previous papers of this series, is reformulated in an approximate SCF scheme. It is shown that the basic features of the one-electron formalism can be retained in the many-electron model for closed shells if the change in π-electron energy due to nuclear displacements is considered to arise from a one-electron perturbation. The modified theory is applied to alternant hydrocarbons. Previous conclusions regarding the importance of second-order bond fixation in monocyclic and benzenoid hydrocarbons are essentially confirmed, whereas the prediction that second-order effects become important also in long polyene chains is shown to have been an artifact of the one-electron model.

In previous papers of this series[3-5] a general theory of double-bond fixation was developed in the framework of a one-electron model and applied to linear, cyclic, benzenoid, and nonalternant hydrocarbons. It was shown that second-order bond distortions can be examined by comparing the largest negative eigenvalue, Λ_{max}, of a matrix, whose elements are the second partial derivatives of the π-electron energy with respect to the bond lengths, with the curvature of the σ potential. If the magnitude of Λ_{max} exceeds a critical value Λ_{crit}, the molecule is predicted to suffer second-order distortions, in a static or dynamic sense, and the distortion pattern is determined by the normalized components of the eigen-

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[1] (a) Alfred P. Sloan Research Fellow; (b) AEC Summer Research Participant, 1968.

[2] The Radiation Laboratory is operated by the University of Notre Dame under contract with the U. S. Atomic Energy Commission. This is AEC Document No. COO-38-634.

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