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Electron Spin Resonance Spectrum of

Tetrakis(p-methoxyphenyl)ethylene Cation Radical

by Jorge A. Valenzuela and Allen J. Bard[1]

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The electron spin resonance (esr) spectrum of the tetrakis(p-methoxyphenyl)ethylene (TAE) cation radical, prepared by treatment with methanesulfonic acid with methylene chloride as a solvent, is given. The experimental coupling constants were found to be in good agreement with those calculated using molecular orbital theory, assuming non-planarity of the molecule, with the methoxyphenyl groups rotated out of the plane of the ethylenic bond by about 32°. A semiempirical approach proposed by Adrian to calculate the theoretical twist angle yielded a value of 34°.

Several years ago, Buck, *et al.*,[2] observed that tetrakis(p-methoxyphenyl)ethylene (tetra-p-anisylethylene or TAE) reacted with bromine to form a blue solution which exhibited an undescribed esr signal. At the
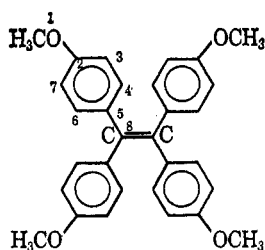
same time, Buckles and Womer[3] studied, spectrophotometrically, the interaction of bromine with TAE in ethylene chloride, and the blue solution obtained was attributed to the formation of donor–acceptor complexes, where TAE was the electron donor. Later, Buckles, *et al.*,[4] described in detail the interaction of TAE with several electron acceptors, observing the characteristic blue solution. Buck, *et al.*,[5] in a study of the system Lewis acid (aluminum chloride)–nitro compound (nitromethane) as a strong electron acceptor, reported that the reaction of TAE with this system produced a divalent positive ion yielding an identical ultraviolet absorption spectrum to that of the perchlorate salt in nitromethane.

The rather easy formation of this diamagnetic dipositive ion with a number of oxidants leads to difficulty in preparing the cation radical of TAE in the absence of appreciable amounts of either parent or dication. The result is that most esr spectra arising from the oxidation of TAE are characterized by a broad unresolved singlet, probably arising from rapid electron exchange between the radical and dipositive cation. Similar effects have been noted in esr studies of hydrocarbon cation radicals.[6]

This study was undertaken to investigate what conditions would lead to a well-resolved spectrum of TAE radical cation, and as a part of a study of the effects of configuration on esr spectra.[7] No previous interpretation of the esr spectrum of TAE cation radical has been reported.[8]

Results and Discussion

Preparation of TAE Cation Radical. A systematic investigation of a number of reported techniques for oxidation of aromatic hydrocarbons was undertaken in an attempt to find conditions for optimum resolution in the esr spectrum of TAE. When the antimony pentachloride in methylene chloride solution oxidation method[6] was employed, only a single broad line with no trace of resolved hyperfine structure was observed. Oxidation with concentrated sulfuric acid[9] produced a spectrum with a small amount of resolution, but it was still not sufficient for a satisfactory analysis. Malachesky, Marcoux, and Adams[10] recently demonstrated

(1) To whom all correspondence and requests for reprints should be directed.

(2) H. M. Buck, J. H. Lupinski, and L. I. Oosterhoff, *Mol. Phys.*, **1**, 196 (1958).

(3) R. E. Buckles and W. D. Womer, *J. Am. Chem. Soc.*, **80**, 5055 (1958).

(4) R. E. Buckles, R. E. Erickson, J. D. Snyder, and W. B. Person, *J. Am. Chem. Soc.*, **82**, 2444 (1960).

(5) H. M. Buck, W. Bloemhoff, and L. J. Oosterhoff, *Tetrahedron Letters*, **9**, 5 (1960).

(6) I. C. Lewis and L. S. Singer, *J. Chem. Phys.*, **43**, 2712 (1965)

(7) (a) L. O. Wheeler, K. S. V. Santhanam, and A. J. Bard, *J. Phys. Chem.*, **70**, 404 (1966); (b) *ibid.*, **71**, 2223 (1967).

(8) Professor Robert E. Buckles, University of Iowa, Iowa City, Iowa, reported in a private communication, 1966, the observation of a 59-line spectrum during the oxidation of TAE.

(9) (a) S. I. Weissman, E. De Boer, and J. J. Conradi, *J. Chem. Phys.*, **26**, 963 (1957); (b) G. J. Hoijtink and W. P. Weijland, *Rec. Trav. Chem.*, **76**, 836 (1957).

(10) P. A. Malachesky, L. S. Marcoux, and R. N. Adams, *J. Phys. Chem.*, **70**, 2064 (1966).
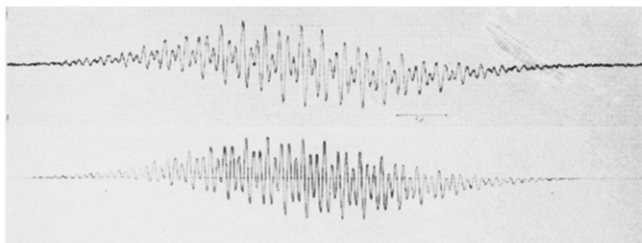
Figure 1. (a) Top: esr spectrum of TAE cation radical produced by methanesulfonic acid oxidation in methylene chloride. The sweeping field is increasing from the left to the right. (b) Bottom: calculated spectrum using constants given in the last row of Table I with a line width of 0.084 gauss.

that 1 M methanesulfonic acid in nitrobenzene solution was a useful solvent for oxidations of aromatic hydrocarbons. The use of methanesulfonic acid as an oxidant employing methylene chloride as a solvent, because of higher solubility of TAE in it, produced a well-resolved spectrum of approximately 67 lines (Figure 1). Electrochemical oxidation of 10^{-4} M solutions of TAE in vacuum-degassed methylene chloride–0.2 M tetra-n-butylammonium perchlorate solutions at a platinum electrode showed esr spectra with some hyperfine structure, which were the same as poorly resolved spectra obtained from the methanesulfonic acid oxidation.

Assignment of Spectrum. The following assignment of coupling constants (in gauss) has been made: $a_H(1) = 0.43 \pm 0.02$ (12 hydrogens), $a_H(3,7) = 0.28 \pm 0.02$ (8 hydrogens), and $a_H(4,6) = 1.16 \pm 0.02$ (8 hydrogens).[11] All anisyl groups are assumed equivalent in the molecule. A computer-simulated spectrum using these coupling constants and assuming a line width of 84 mgauss and 100% Lorentzian line shape is also shown in Figure 1.

Molecular Orbital Calculations. In order to correlate the experimental splitting assignments with a theoretical molecular model, calculations of π-e spin density were performed using simple Hückel LCAO–MO[12,13] and McLachlan MO–SCF[14] procedures. The McLachlan method is an approximate self-consistent configuration-interaction modification of the Hückel LCAO–MO method.

Two problems arise in carrying out these calculations. The first involves assignment of the coulomb integral (α_O) and the resonance integral (β_{CO}) associated with the oxygen atoms. The second involves accounting for the steric interactions between the o-hydrogens on the anisyl groups, which force the molecule out of a planar configuration.

Coulomb and Resonance Integrals. The values of α_O and β_{CO} are generally given by equations of the following type[13]

$$\alpha_{CO} = \alpha_C + \delta_O\beta_{CC}$$

$$\beta_{CO} = \gamma_{CO}\beta_{CC}$$

where α_C and β_{CC} are the coulomb and resonance integrals, respectively, for benzene, and δ_O and γ_{CO} are the coulomb and resonance integral parameters (sometimes denoted h_O and k_{CO}[13]). We have employed the values $\delta_O = 2.0$ and $\gamma_{CO} = 0.8$, suggested by Streitwieser[13] and used by Zweig, Hodgson, and Jura,[15] in correlating esr and polarographic data of methoxybenzenes. Pullman[16] has suggested similar parameters ($\delta_O = 2.0$, $\gamma_{CO} = 0.9$). Walter[17] has recently proposed quite different values of these parameters, based on optimization of parameters for fitting esr coupling constants in 1-picryl-2,2-bis(p-methoxyphenyl)hydrazyl and related compounds. Because of the number of adjustable parameters which had to be employed in this optimization, we feel Walter's values are less applicable to the present work.

The oxygen also modifies the coulomb integral on carbon 2 (α_2) by an inductive or direct effect, which is sometimes taken into account by equations such as

$$\alpha_2 = \alpha_C + \delta_C'\beta_{CC}$$

with $\delta_C' = \delta\delta_O$, where δ, the auxiliary inductive parameter, is given values in the order of 0.1. In this study, δ_C' was taken as zero. The $-OCH_3$ group is regarded as $-\ddot{O}$, contributing two electrons to the π system.[18]

The resonance integral parameter for the ethylenic double bond, $\gamma_{C=C}$, was assigned a value of 1.1. This parameter was calculated from the relation between the bond order and the bond length of a bond by the equation

$$r_{ij} = a - bp_{ij}$$

where r_{ij} is the bond length between atom i and j, p_{ij} is the corresponding bond order, and a and b are adjustable parameters.[19] The parameters suggested by Coulson and Golembiewski,[20] $a = 1.517$ and $b = 0.180$, were employed. From the bond length, we estimated $\gamma_{C=C}$ using the relation of Mulliken.[13,21] We repeated this procedure until a self-consistent bond

(11) The assignment of this spectrum is not unique, and other combinations of proton coupling constants for 8,8,12 or even 4,4,6 could probably fit the spectrum as well. The proposed assignment is mainly based on molecular-orbital calculations.

(12) E. Hückel, *Z. Physik*, **70**, 204 (1931).

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

(14) A. D. McLachlan, *Mol. Phys.*, **3**, 233 (1960).

(15) A. Zweig, W. G. Hodgson, and W. H. Jura, *J. Am. Chem. Soc.*, **86**, 4124 (1964).

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(19) L. Salem, "The Molecular Orbital Theory of Conjugated Systems," W. A. Benjamin, Inc., New York, N. Y., 1966, pp 137, 138.

(20) C. A. Coulson and A. Golembiewski, *Proc. Phys. Soc.*, **78**, 131 (1961).

(21) R. S. Mulliken, *J. Chim. Phys.*, **46**, 375 (1949); R. S. Mulliken, C. A. Rieke, D. Orloff, and H. Orloff, *J. Chem. Phys.*, **17**, 1248 (1949); R. S. Mulliken, *J. Phys. Chem.*, **56**, 295 (1952).

length was obtained, and found a bond order of 0.8519 and a bond length of 1.364 Å. We should point out that the choice of relation between the resonance integral and the bond length does not significantly affect the results, and the differences in the value of $\gamma_{C=C}$ obtained with different procedures are below the limits of accuracy of our calculations. These calculations were done assuming planar configuration. The small changes in the C=C bond length when the molecule is considered nonplanar are too small to affect the value of the resonance integral significantly.

Steric Effects. Steric strain caused by repulsion of the orthohydrogens (*i.e.*, 4,6), especially between the anisyl groups located on the different ethylene carbons, can be alleviated by stretching or bending of the anisylethylene carbon (C_5–C_8) bonds, by rotation about the C_5–C_8 bonds, and by rotation about the ethylenic bond. The calculation performed here assumes all of the steric strain is relieved by rotation about the C_5–C_8 bonds. A similar assumption has been used in calculations involving phenyl-substituted anthracenes[7] and is somewhat justified by the calculations of Favini and Simonetta.[22] Even admitting only rotation about the C_5–C_8 bonds, the strain can be eased by a small rotation of all of the anisyl groups out of the plane of the ethylene bond or by a larger displacement of the two *trans*-related anisyl groups leaving the two remaining *trans*-anisyl groups in the plane of the ethylene bond. Jones[23] favored the second possibility in a study which compared the ultraviolet absorption spectrum of tetraphenylethylene with that of *trans*-stilbene. However, in a more detailed analysis of the spectra by the molecular orbital method, Suzuki[24] found that the configuration in which all groups are rotated out the plane of the ethylenic bond was a more reasonable one. Favini and Simonetta[22] employed a similar model with good success. Therefore, a model in which all anisyl groups are equivalent was adopted here. The resonance integral for the C_5–C_8 bond (β_θ) was evaluated from the equation $\beta_\theta = \beta_{\theta=0} \cos \theta$,[7,25,26] where $\beta_{\theta=0}$ is the value of the resonance integral in the planar configuration at the same internuclear distance. The bond order and bond length for the C_5–C_8 bond was calculated in the same manner as that of the C=C bond. From these values, 0.2775 and 1.464 Å, a value of $\beta_{\theta=0} = 0.9 \ \beta_{CC}$ was obtained. The McLachlan[14] calculations were carried out following the Hückel MO calculations, employing a λ value of 1.10.

Results. Values of the spin densities (ρ) were calculated for various θ values; typical results based on a Hückel MO calculations are shown in Figure 2. The calculated ρ values were compared with those derived from the experimental coupling constants (a_H) using: McConnell's relation,[27] $a_H = Q\rho$, with $Q = 35.7$, calculated by Lewis and Singer[6] using a least-squares fitting procedure for about 12 cation radicals; Colpa–Bolton's relation,[28,29] $a_H = -(Q\rho \pm K\rho^2)$, where $Q =$
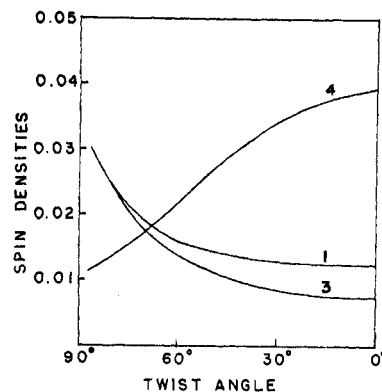
Figure 2. Plot of the Hückel spin densities as a function of the twist angle (θ) for TAE. The numbers correspond to the positions of atoms in the TAE molecule.

Table I

	Position		
	1	3	4
Hückel spin density[a]	0.0128	0.0085	0.0337
McLachlan spin density[b]	0.0088	−0.0075	0.0416
$|a_H|$, gauss[c]	0.46	0.30	1.20
$|a_H|$, gauss[d]	0.31	0.27	1.49
$|a_H|$, gauss[e]	0.35	0.23	0.92
$|a_H|$, gauss[f]	0.24	0.20	1.14
$|a_H|$, gauss[g]	0.58	0.29	1.16
Experimental a_H, gauss	0.43 ± 0.02[h]	0.28 ± 0.02[h]	1.16 ± 0.02

[a] Calculated using $\theta = 32°$. [b] Calculated using $\theta = 32°$ and $\lambda = 1.1$. [c] Calculated using the McConnell equation, where $Q = 35.7$, and Hückel spin densities. [d] Calculated using the McConnell equation, where $Q = 35.7$, and McLachlan spin densities. [e] Calculated using the Colpa–Bolton equation, where $Q = 27$ and $K = 12$, and Hückel spin densities. [f] Calculated using the Colpa–Bolton equation, where $Q = 27$ and $K = 12$, and McLachlan spin densities. [g] Calculated using the Giacometti, et al., equation, where $Q_1 = 31.5$ and $Q_2 = 7$, and Hückel spin densities. [h] Assigned to this position on the basis of analogy with Hückel molecular-orbital theory.

27 and $K = 12$; and Giacometti, Nordio, and Pavan's relation,[30] $a_H = Q_1\rho \pm Q_2 |\sum_i c_i c_j|$, where $Q_1 = 31.5$ and $Q_2 = 7$.

The calculated values are shown in Table I. It was

(22) G. Favini and M. Simonetta, *Theoret. Chim. Acta*, 1, 294 (1963).
(23) R. N. Jones, *J. Am. Chem. Soc.*, 65, 1818 (1943).
(24) H. Suzuki, *Bull. Chem. Soc. Japan*, 33, 389 (1960).
(25) H. Preuss, *Z. Naturforsch.*, 12a, 603 (1957).
(26) M. J. S. Dewar, *J. Am. Chem. Soc.*, 74, 3345 (1952).
(27) H. M. McConnell, *J. Chem. Phys.*, 24, 632, 764 (1956); H. M. McConnell and H. H. Dearman, *ibid.*, 28, 51 (1958); H. M. McConnell and D. B. Chesnut, *ibid.*, 28, 107 (1958).
(28) J. P. Colpa and J. R. Bolton, *Mol. Phys.*, 6, 273 (1963).
(29) J. R. Bolton, *J. Chem. Phys.*, 43, 309 (1965).
(30) G. Giacometti, P. L. Nordio, and M. V. Pavan, *Theoret. Chim. Acta*, 1, 404 (1963).

found that the best fit between experimental and theoretical coupling constants is obtained when the methoxyphenyl groups are rotated out of the plane of the ethylenic bond by about 32°. The technique of comparing the ratio of the experimental coupling constants with the ratio of the corresponding spin densities at different values of the angle θ^7 also yields an angle of about 32°.

Molecular Geometry of TAE

We have already pointed out that TAE cannot have a planar structure because of steric hindrance. This steric effect in overcrowded molecules has been studied extensively[22,31-35] and many theoretical procedures have been proposed to calculate their structures. Most of these procedures consider that this steric strain can be released by a twisting around a C–C bond. We have similarly assumed, in the case of TAE, that this steric strain can be released by rotation of the anisyl groups out of the plane of the ethylenic bond.

To calculate the steric interaction energy in TAE, we have used a method proposed by Eyring[36,37] based on the valence bond approximation of perfect pairing. According to this procedure, the steric interaction for two hydrogen atoms is given by the equation

$$E_s = \frac{1}{4}{}^1\Sigma + \frac{3}{4}{}^3\Sigma$$

where E_s is the steric interaction energy, and $^1\Sigma$ and $^3\Sigma$ are the energies of the lowest single and triplet states of the hydrogen molecule.[33] These energies are known as a function of the internuclear separation.[38]

Adrian[31] calculated the geometrical configuration of triphenylmethyl, biphenyl, stilbene, and azobenzene using the Eyring method to get the steric interaction energy and the valence bond method to obtain the resonance energy. He plotted the steric and resonance energies as functions of the twist angle and added them together; the minimum of this resulting energy yielded the effective resonance energy at the equilibrium angle. In general, we followed the same procedure here, but calculating the resonance energies using the Hückel molecular orbital method. To calculate the resonance energies we use the equation

$$E_r' \text{ (twist angle)} = E_r \text{ (twist angle)} - E_r \text{ (90°)}$$

where we actually obtain the difference in resonance energy between a partially and completely twisted molecule.[31] The effective resonance energy E_t will be the addition of E_s and E'_r at the different θ. These energies are given in Figure 3. This treatment, therefore, predicts the anisyl groups in TAE are rotated out of the plane by an angle of about 34°, and the effective resonance energy is about −7 kcal/mole.[39] A similar treatment has been use for phenyl-substituted anthracenes, with a discussion of the limitation of the approach.[40]
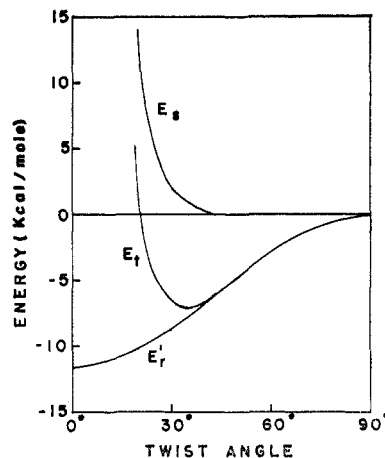

Figure 3. The steric energy (E_s), the resonance energy (E_r'), and the effective resonance energy (E_t) for the TAE as functions of the twist angle.

Conclusions

The angle obtained by the theoretical approach and by esr agree very well within the limits of accuracy of these calculations. Considering all the approximations performed both in the theoretical approach and in the Hückel molecular orbital method to correlate the esr coupling constants, we conclude that, at first approximation, the most stable configuration for TAE involves the anisyl groups rotated out of the plane of the ethylenic bond by about 32°. A very recent publication by Baenziger, Buckles, and Simpson[41] on the crystal structure of the dichloroiodiate (I) salt of the tetra-p-anisylethylene dication showed that the anisyl groups are rotated 28.2° out of the plane of the ethylenic bond in the crystal structure.

Experimental Section

TAE was provided by Dr. E. A. Chandross (Bell Laboratories) and was used as received; its purity was established by carbon–hydrogen analysis, visible and ultraviolet spectroscopy, and melting point determination. Methanesulfonic acid and methylene chloride

(31) F. J. Adrian, J. Chem. Phys., 28, 608 (1958).

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(33) C. A. Coulson and C. W. Haigh, Tetrahedron, 19, 527 (1963).

(34) A. Golebiewski and A. Parczewski, Theoret. Chim. Acta, 7, 171 (1967).

(35) T. H. Goodwin and D. A. Morton-Blake, ibid., 1, 458 (1963).

(36) H. Eyring, J. Am. Chem. Soc., 54, 3191 (1932).

(37) C. A. Coulson, "Valence," 2nd ed, Oxford University Press, London, 1961, p 174.

(38) J. O. Hirschfelder and J. W. Linnett, J. Chem. Phys., 18, 130 (1950).

(39) The β used in this work was that also used by Adrian (see ref 31), −17 kcal/mole. See G. W. Wheland, "Resonance in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1955, p 132.

(40) L. O. Wheeler, Ph.D. Dissertation, The University of Texas, 1967.

(41) N. C. Baenziger, R. E. Buckles, and T. D. Simpson, J. Am. Chem. Soc., 89, 3405 (1967).

were obtained from Aldrich Chemical Co. and were used without further purification.

The cation radical was prepared by dissolving about 10–15 mg of TAE in 1–2 ml of methylene chloride and treating this solution with 2–3 ml of methanesulfonic acid. A red solution is produced. The solution was stirred for at least 10 min and nitrogen was bubbled through it. The solution was then transferred to a flat Varian aqueous sample cell. This red solution obtained was very stable, lasting at least 1 week. The reaction of TAE with sulfuric acid, on the other hand, leads very quickly to a blue color.

A Varian Associates V-4502 spectrometer employing 100-kc field modulation and a Varian V-153C Klystron (output, 300 mW) were used. The field sweep was calibrated by using Fremy's salt in one side of a V-4532 dual sample cavity. The high and the low field coupling constants for the Fremy's salt were taken as

13.160 ± 0.008 and 13.101 ± 0.004, based on measurements obtained in this laboratory by Mr. T. V. Atkinson.

The Hückel and McLachlan molecular orbital calculations were done on a Control Data Corp. 6600 computer. The theoretical simulated spectrum was calculated on the CDC computer and plotted on the CDC 160 plotter.

Carbon-13 Nuclear Magnetic Resonance Studies of 3-Substituted Pyridines

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Carbon-13 magnetic shieldings for eight 3-substituted pyridines are reported and compared with those of the corresponding monosubstituted benzenes. Thirty of the forty carbon shieldings measured in the spectra of the pyridines yield substituent effects that are within ±1.3 ppm of those found for the benzenes. Shieldings of the carbons in the 6 position in the pyridines are shown to reflect electron release or withdrawal by substituent groups.

Introduction

Carbon-13 magnetic shieldings in substituted benzenes have recently received considerable attention.[1] The effects of substituents on ring carbon shieldings are nearly additive, except in cases where steric interactions are pronounced, and often reflect specific electronic properties of the substituents. No corresponding studies of six-membered aromatic ring heterocyclic molecules have been reported, although data for azines and selected methylazines[2] and protonated diazines[3] have appeared. A C^{13} nmr study of monosubstituted pyridines was undertaken in this laboratory to determine whether or not these compounds could be treated analogously to the benzenes. We wish here to report carbon shieldings for eight 3-substituted pyridines which constitute the second phase of this investiga-

tion. Substituents studied included weak electron-releasing groups and moderate to strong electron-attracting groups. Pyridines bearing strong electron-releasing groups in the 3-position were not studied since these were either not available or not sufficiently soluble in suitable solvents for C^{13} nmr studies. A similar study of 4-substituted pyridines has recently been reported.[4]

(1) Numerous papers reporting carbon shieldings in substituted benzenes have appeared. Typical examples are: (a) H. Spiesecke and W. G. Schneider, *J. Chem. Phys.*, **35**, 731 (1961); (b) P. C. Lauterbur, *J. Am. Chem. Soc.*, **83**, 1838 (1961); (c) K. S. Dhami and J. B. Stothers, *Can. J. Chem.*, **43**, 479 (1965); (d) G. B. Savitsky, *J. Phys. Chem.*, **67**, 2723 (1963); (e) G. E. Maciel and J. J. Natterstad, *J. Chem. Phys.*, **42**, 2427 (1965).

(2) P. C. Lauterbur, *ibid.*, **43**, 360 (1965).

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(4) H. L. Retcofsky and R. A. Friedel, *J. Phys. Chem.*, **71**, 3592 (1967).