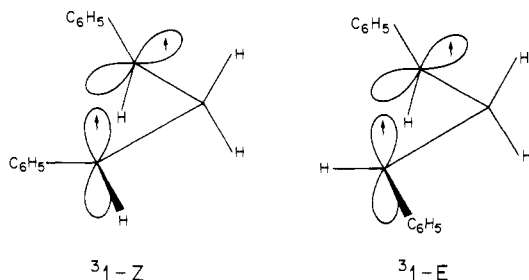


the planar intermediate (6) should provide a ready pathway for isomerization since it could collapse to regenerate either the *cis*- or the *trans*-cyclopropane. Accordingly, the involvement of structure 6 can be expected to result in polarized isomerization products. The alternative structure (5), on the other hand, cannot be expected to permit ready isomerization but should preserve the steric integrity of the reactant. In view of these considerations, the failure to observe polarized rearrangement products identifies the nonplanar radical cation (5) as the intermediate in which the polarization is generated.

The lack of isomerization during the photoreaction of 1 and 2 stands in marked contrast to the reaction of 1 with acceptors such as 1,4-dicyanonaphthalene (8), suggesting a principally different reaction mechanism. Wong and Arnold applied the CIDNP technique to study the reaction of *trans*-1 with 8.<sup>11</sup> They observed a single, apparently weak A/E multiplet which they assigned to the benzylic resonance of *cis*-1. On the basis of this result, they postulated a mechanism involving electron transfer from 1 to 8 and triplet recombination<sup>15</sup> of the resulting radical ion pair. The energetics of the system are not inconsistent with the proposed mechanism.<sup>16</sup> However, the observation of only one signal fails to identify the structure of the postulated radical cation and leaves questions concerning the polarization mechanism unanswered.

In view of the recent interest in the recombination of triplet pairs,<sup>15</sup> it appeared desirable to have the benefit of additional experimental evidence. Accordingly, we extended our study to include the reactions of 1,4-dicyanonaphthalene (8) and 9-cyanophenanthrene (9) with 1.<sup>16</sup> The irradiation of 8 in the presence of *trans*-1 resulted in CIDNP effects for all signals of reactant as well as rearranged cyclopropanes. A/E multiplet polarization was observed for the benzylic protons of the *cis* isomer and E/A polarization was observed for the benzylic protons of *trans*-1. The signals of the geminal protons of *cis*- and *trans*-1 overlap, but a detailed analysis reveals A/E polarization for the *cis* isomer and E/A polarization for the *trans* isomer (Figure 2, top). The reaction of 9 with *trans*-1 resulted in the exclusive polarization of the *cis* isomer (Figure 2, bottom).

These results are compatible with the mechanism suggested by Wong and Arnold but they also elucidate the structure of the intermediate radical ion and they reveal the presence of singlet recombination. Electron-transfer quenching of the excited-singlet acceptors ( $\mu < 0$ ) generates the open cyclopropane radical cation (5) paired with acceptor anions of similar  $g$  factors ( $\Delta g \sim 0$ ). The reactant is regenerated by geminate electron return in singlet pairs ( $\epsilon > 0$ ), whereas the rearranged cyclopropane is formed via triplet recombination yielding a triplet state ( $^3Z$  or  $^3E$ ) with orthogonal  $p$  orbitals. This intermediate can decay to the ground



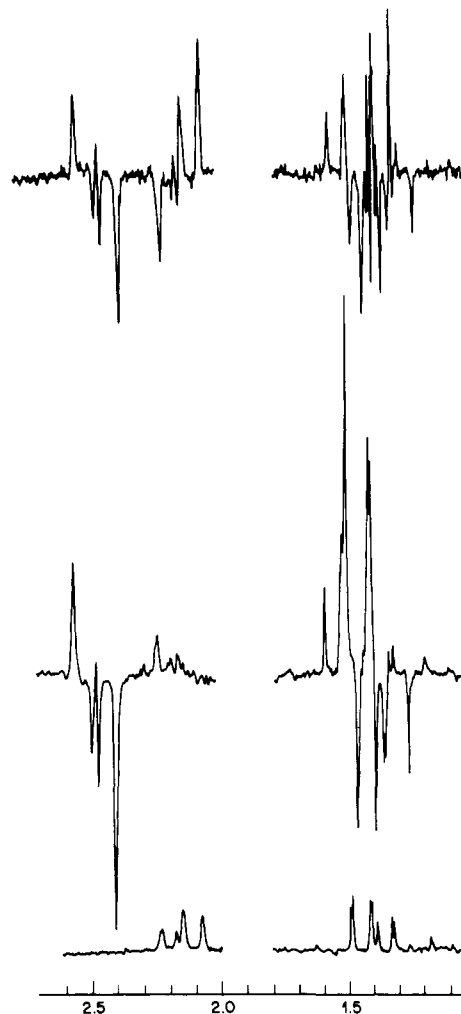
(15) (a) Ottolenghi, M. *Acc. Chem. Res.* **1973**, *6*, 153. (b) Orbach, N.; Ottolenghi, M. *Chem. Phys. Lett.* **1975**, *35*, 175. (c) In "The Exciplex"; Gordon, M., Ware, W. R., Eds.; Academic Press: New York, 1975; p 25. (d) Michel-Beyerle, M. E.; Haberkorn, R.; Bube, W.; Steffens, E.; Schröder, H.; Neusser, N. J.; Schlag, E. W.; Seidlitz, H. *Chem. Phys.* **1976**, *17*, 139. (e) Schulten, C. K.; Staerk, H.; Weller, A.; Werner, H. J.; Nickel, B. *Z. Phys. Chem. (Wiesbaden)* **1976**, *101*, 371. (f) Closs, G. L.; Czeropski, M. S. *J. Am. Chem. Soc.* **1977**, *99*, 6127. (g) Bargon, J. *Ibid.* **1977**, *99*, 8351.

(16) The reduction potentials of 8,  $E_{(A^-/A)} \sim -1.3$  V,<sup>17</sup> and 9,  $E_{(A^-/A)} = -1.92$  V vs. SCE,<sup>18</sup> would place the pair energy above the triplet energy of 1 ( $E_T \sim 50$ -60 kcal/mol).<sup>19</sup>

(17) Arnold, D. R.; Maroulis, A. *J. Am. Chem. Soc.* **1976**, *98*, 5931.

(18) Park, S. M.; Caldwell, R. A. *J. Electrochem. Soc.* **1977**, *124*, 1859.

(19) Becker, R. S.; Edwards, L.; Bost, R.; Elam, M.; Griffin, G. *J. Am. Chem. Soc.* **1972**, *94*, 6584.



**Figure 2.**  $^1\text{H}$  NMR spectra (90 MHz) observed during the irradiation of 9-cyanophenanthrene (0.02 M; center) or of 1,4-dicyanonaphthalene (0.02 M; top) in acetonitrile- $d_3$  solutions containing 0.02 M *trans*-diphenylcyclopropane. A dark spectrum of the cyclopropane is shown as the bottom trace.

state of either geometric isomer. Accordingly, the polarization due to triplet recombination is partitioned between reactant and rearranged cyclopropane, thus weakening the singlet return polarization of the reactant.

The finding that in the reaction of 9 the polarization of the rearranged cyclopropane is stronger than that of the reactant is interpreted as evidence that triplet recombination can be more efficient than singlet recombination, a trend which has been invoked repeatedly in recent years.<sup>15</sup> Photoreactions of arylcyclopropanes with fixed geometries and of related diphenylcyclobutane compounds are presently under investigation to further delineate the mechanisms and structures discussed in this paper.

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### Why Is Tetra-*tert*-butylcyclobutadiene Almost Square?

Sir:

The X-ray structures of three derivatives of cyclobutadiene (CBD) have been published, and the bond lengths found in the four-membered ring of each are reproduced in Figure 1. As shown, the near equality of the ring bond lengths in the tetra-

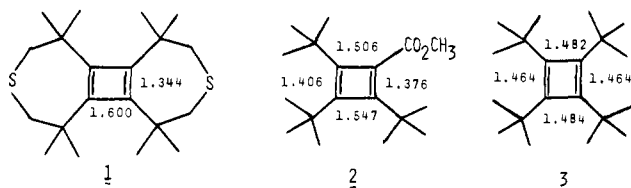


Figure 1. Bond lengths (Å) in three CBD derivatives.

*tert*-butyl-substituted molecule (3)<sup>1</sup> stands in contrast to the pronounced bond alternation exhibited by 1<sup>2</sup> and 2.<sup>3</sup> In fact, were it not for recent spectroscopic,<sup>4</sup> chemical,<sup>5</sup> and theoretical<sup>6-8</sup> results, it might be inferred from the X-ray structure of 3 that the parent CBD was square or nearly so.

In this communication we present the results of *ab initio* calculations on CBD. These results and the accompanying theoretical analysis provide an explanation of the nearly square geometry of 3.

We begin by noting that the observed trend in double bond lengths along the series 1-3 can be attributed to differences in steric interactions between substituents. In 1, where strong steric interactions exist along only two distal ring bonds, the double bond lengths are quite normal. In 2 increased steric interactions between the substituents on the double bonds leads to a pronounced lengthening. Replacement of the carbomethoxy group in 2 by a fourth *tert*-butyl group in 3 leads to further lengthening of the double bonds.

Steric interactions between neighboring groups often have both structural and energetic consequences.<sup>9</sup> However, the magnitude of 0.12 Å for the change in double bond length along the series 1-3 is most unusual. That the size of this change is, indeed, extraordinary can be appreciated from the fact that the two bonds joining the substituted carbons in 1,2,4,5-tetra-*tert*-butylbenzene are only 0.02 Å longer than the remaining four.<sup>10</sup> Apparently, steric interactions lead to much greater lengthening of the double bonds in cyclobutadiene than of the *partial* double bonds in benzene.<sup>11</sup>

Although the magnitude of the change in the double bond lengths in the series 1-3 is dramatic, even more startling is the fact that increased steric interaction between substituents along the double bonds leads to concomitant *shortening* of the other two ring bonds. One might have expected these latter bonds in 3 to remain essentially the same length as the single bonds in 1. Instead, the "single" bonds in 3 are fully 0.12 Å shorter than those in 1, a change of the same size but of opposite direction to the change that occurs in the double bond lengths.

We have carried out  $\pi$  CI calculations with an STO-3G basis set<sup>12</sup> on the parent CBD in order to understand (a) the large magnitude of the increase in double bond lengths that is apparently induced by steric interactions between substituents and (b) why this increase is accompanied by shortening of the single bonds,

(1) Irngartinger, H.; Riegler, N.; Malsch, K. D.; Schneider, K. A.; Maier, G. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 211.

(2) Irngartinger, H.; Rodewald, H. *Angew. Chem., Int. Ed. Engl.* **1974**, *13*, 740.

(3) Delbaere, L. R. J.; James, M. N. G.; Nakamura, N.; Masamune, S. *J. Am. Chem. Soc.* **1975**, *97*, 1973.

(4) Masamune, S.; Souto-Bachiller, F. A.; Machiguchi, T.; Bertie, J. E. *J. Am. Chem. Soc.* **1978**, *100*, 4889.

(5) Whitman, D. W.; Carpenter, B. K., *J. Am. Chem. Soc.* **1980**, *102*, 4272.

(6) Kollmar, H.; Staemmler, V. *J. Am. Chem. Soc.* **1977**, *99*, 3583.

(7) Borden, W. T.; Davidson, E.; Hart, P. *J. Am. Chem. Soc.* **1978**, *100*, 388.

(8) Jafri, J. A.; Newton, M. *J. Am. Chem. Soc.* **1978**, *100*, 5012.

(9) Review: Liebman, J.; Greenberg, A. *Chem. Rev.* **1976**, *76*, 311.

(10) van Bruijnsvoort, A.; Eilerman, L.; van der Meer, H.; Stam, C. H. *Tetrahedron Lett.* **1968**, 2527.

(11) It can be argued that an increase in steric buttressing in going from 1 to 3 may be partially responsible for this effect. On the other hand, the larger angles between the *tert*-butyl groups and the ring bonds in 3 than in 1,2,4,5-*tert*-butylbenzene should make steric interactions between these groups less severe in the CBD than in the benzene derivative.

(12) Hehre, W. J.; Stewart, R. F.; Pople, J. A. *J. Chem. Phys.* **1969**, *51*, 2657. Molecular orbitals for the CI were defined by two-configuration MCSCF calculations.

Table I. Optimal Single Bond Lengths for Fixed Values of the Double Bond Lengths in Singlet CBD

$r_{C=C}$ , Å	$r_{C-C}$ , Å	$E$ , kcal/mol
1.368	1.543	0 <sup>a</sup>
1.410	1.525	1.6
1.433	1.504	3.3
1.453	1.453	4.3

<sup>a</sup>  $E = -151.8477$  hartree at the optimal STO-3G,  $\pi$  CI geometry for rectangular CBD.<sup>7</sup>

a change that enlarges the steric interactions between the substituents along these two bonds. We find at the  $\pi$  CI level of theory that the energetic cost of lengthening the two double bonds in CBD from their equilibrium value of 1.368 Å to 1.453 Å, the optimal bond length for a square geometry,<sup>7</sup> is only 6.5 kcal/mol. This modest energy increase is reduced to 4.6 kcal/mol when the single bonds are allowed to relax from 1.543 Å, their length at the rectangular equilibrium geometry, to their optimal value for a double bond length of 1.453 Å. As shown in Table I, when the double bonds in CBD are lengthened, the single bonds preferentially shorten. In fact, when one pair of bond lengths is fixed at 1.453 Å, the optimal length for the other pair of bonds is found also to be 1.453 Å; a square geometry becomes preferred to a rectangular one.<sup>13</sup>

The physical reason why single bond shortening accompanies double bond lengthening in CBD has its origin in the fact that, although  $\pi$  bonding (in the Hückel sense) is maximized at a rectangular geometry, electron repulsion and the energy of the  $\sigma$  ring bonds are minimized at a square one.<sup>14</sup> Consequently, if  $\pi$  bonding is disrupted by lengthening the double bonds, the molecular geometry relaxes by single bond shortening toward a square, and the increase in energy over that at the optimal rectangular geometry is small.

The  $\pi$  CI value of 4.2 kcal/mol for the energy difference between square and rectangular CBD is probably too small, since it has been shown that this number increases with inclusion of CI in the  $\sigma$  space.<sup>7,8</sup> Nevertheless, the best current theoretical estimates of this energy difference are only about 10 kcal/mol.<sup>6-8</sup> Therefore, double bond lengthening, accompanied by single bond shortening, is predicted to provide a facile mode of relieving steric compression between substituents on the double bonds of CBD.

Although it is certainly true that shortening the single bonds increases the steric interactions between substituents along them, the lowest energy mode for lengthening the double bonds is one that involves simultaneous shortening of the single bonds. This fact is evident not only in the results of our calculations, summarized in Table I,<sup>15</sup> but also in the near constancy of the sum of the single and double bond lengths in 1-3. If the CBD potential surface imposes this constraint on the bond lengths and if the repulsive potential between substituents varies as  $(a+r)^{-n}$ , it is easy to show that the repulsive energy between substituents is minimized at a square geometry.

At the equilibrium geometry of a substituted CBD it is not the repulsive energy between substituents that is minimized, but the total energy. Nevertheless, in 3 relief of steric compression between substituents apparently supplies a substantial part of the energy required to transform the CBD ring to a square geometry.

(13) Since this  $D_{4h}$  geometry is a stationary point on the energy surface, the energy around this point can be expressed in the form  $E = k(x^2 + y^2)/2 + k'xy$  for small distortions,  $x$  and  $y$ , of the two sets of distal bonds from 1.453 Å. Our calculations show that  $k > 0$ . Thus when either  $x$  or  $y = 0$ , the energy is minimized when the other distortion is also zero.

(14) Snyder, L. C. *J. Phys. Chem.* **1962**, *66*, 2299. (b) Borden, W. T. *J. Am. Chem. Soc.* **1975**, *97*, 5968.

(15) It is apparent from the data in the table that the shortening of the single bonds does not proceed at exactly the same rate at which the double bonds are lengthened. One way to understand this fact is to use a quadratic potential<sup>13</sup> to calculate, for a fixed deviation of one set of bonds from their preferred length at the square geometry, the optimal deviation of the other set. Minimization of the energy yields  $y = -k'x/k$ . The large second order Jahn-Teller effect that occurs on distortion of singlet CBD from a square to a rectangular geometry<sup>7,8</sup> causes  $k'$  to be large and  $k$  small. Thus, a modest deviation of  $x$  from zero yields a much larger magnitude of  $y$ .

In CBD derivatives like **3** the barrier to pseudorotation to an equivalent rectangular geometry via a square transition state should therefore be reduced from the roughly 10 kcal/mol that the best ab initio calculations find for the parent molecule.<sup>16</sup> This may explain the absence of line broadening in the <sup>13</sup>C NMR spectrum of the tri-*tert*-butyl derivative of CBD at even very low temperatures.<sup>17</sup>

In summary, our calculations show relatively small energy increases for large increases in the lengths of the double bonds in CBD. The energy increases are minimized if, concomitant with double bond lengthening, single bond shortening occurs. These theoretical findings provide an explanation of the dramatic changes in geometry with increasing steric interactions between substituents on the double bonds in the series 1-3.<sup>18</sup>

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(16) The data in Table I show the fraction of the barrier that is eliminated after partial distortion of CBD from the rectangular minimum toward a square geometry.

(17) Maier, G.; Schafer, U.; Sauer, W.; Hartan, H.; Oth, J. F. M. *Tetrahedron Lett.* **1978**, 1837. This explanation has been suggested by Bally, T.; Masamune, S. *Tetrahedron* **1980**, *36*, 343. An alternative explanation is that C-1 and C-3, which are nonequivalent in a rectangular geometry, nevertheless, have nearly identical chemical shifts.

(18) It should be noted that the geometry and apparent diamagnetic nature of **3** provide evidence for the correctness of the theoretical prediction of a singlet ground state for CBD, even at a square geometry.<sup>6-8,14b,19</sup>

(19) Bunker, R. J.; Peyerimhoff, S. D. *J. Chem. Phys.* **1968**, *48*, 354. Craig, D. P. *Proc. R. Soc. London, Ser. A* **1950**, *202*, 498.

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## Surface-Enhanced Resonance Raman Scattering from Cytochrome *c* and Myoglobin Adsorbed on a Silver Electrode

Sir:

The study of adsorbed molecules on metal surfaces by Raman spectroscopy, once an almost impossible task, has rapidly developed into a major area of interest in recent years. The activity in this field was kindled by the original observation of Raman spectra of pyridine on Ag in an electrochemical cell<sup>1</sup> and the discovery that these spectra were observed only because of the previously unrecognized enhancement of the Raman scattering cross section (approximately 10<sup>6</sup>) by the silver electrode surface.<sup>2</sup> Such spectra have now come to be known as surface-enhanced Raman Spectra (SERS).<sup>3</sup> SERS has been observed for a variety of small neutral molecules (e.g., *N*-heterocycles, aromatic and aliphatic amines,<sup>3</sup> olefins,<sup>4a</sup> CO<sup>4b,c</sup>) and ions (e.g., CN<sup>-</sup>,<sup>5a-d</sup> SCN<sup>-</sup>,<sup>5e-g</sup> N<sub>3</sub><sup>-</sup>, Pt(CN)<sub>4</sub><sup>2-</sup>,

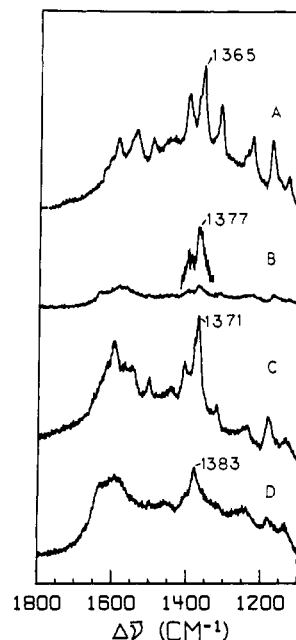
(1) (a) Fleischmann, M.; Hendra, P. J.; McQuillan, A. J. *Chem. Phys. Lett.* **1974**, *26*, 163-166. (b) McQuillan, A. J.; Hendra, P. J.; Fleischmann, M. J. *Electroanal. Chem.* **1975**, *65*, 933-944. (c) Paul, R. L.; McQuillan, J.; Hendra, P. J.; Fleischmann, M. *Ibid.* **1975**, *66*, 248-249. (d) Fleischmann, M.; Hendra, P. J.; McQuillan, A. J.; Paul, R. L.; Reid, E. S. *J. Raman Spectrosc.* **1976**, *4*, 269-274.

(2) Jeanmarie, D. L.; Van Duyne, R. P. *J. Electroanal. Chem.* **1977**, *84*, 1-20.

(3) Van Duyne, R. P. *Chem. Biochem. Appl. Lasers* **1978**, 101-185.

(4) (a) Moscovitz, M.; DiLella, D. *Chem. Phys. Lett.* **1980**, *73*, 500-505. (b) Wood, T. H.; Klein, M. V. *J. Vac. Sci. Technol.* **1979**, *16*, 459-461. (c) Wood, T. H.; Klein, M. V. *Solid State Commun.* **1980**, *35*, 263-265.

(5) (a) Otto, A. *Surf. Sci.* **1978**, *75*, L392-L396. (b) Furtak, T. E. *Solid State Commun.* **1978**, *28*, 903-906. (c) Dornhaus, R.; Long, M. B.; Benner, R. E.; Chang, R. K. *Surf. Sci.* **1980**, *93*, 240-262. (d) Schultz, S. G.; Van Duyne, R. P. *Surf. Sci.*, to be submitted. (e) Cooney, R. P.; Reid, E. S.; Fleischmann, M.; Hendra, P. J. *J. Chem. Soc., Faraday Trans. 1* **1977**, 1691-1698. (f) Gold, H. S.; Buck, R. P. *J. Raman Spectrosc.* **1979**, *8*, 323-325. (g) Allen, C. S.; Van Duyne, R. P. *J. Am. Chem. Soc.*, submitted.



**Figure 1.** Surface-enhanced RR spectra of  $1 \times 10^{-6}$  M sperm whale myoglobin and tuna cytochrome *c* adsorbed on an anodized Ag electrode. (A) Cytochrome *c* at  $-0.6$  V vs. SCE; (B) cytochrome *c* at  $-0.2$  V vs. SCE; (C) myoglobin at  $-0.6$  V vs. SCE; (D) myoglobin at  $-0.2$  V vs. SCE. The excitation wavelength was 514.5 nm and the power was 40 mW. Scan parameters are as follows: slit width =  $2 \text{ cm}^{-1}$ , scan rate =  $0.3333 \text{ \AA/s}$ , and 1.0-s counting interval. For simplicity, only those bands discussed in the text are labeled.

Ru(CN)<sub>6</sub><sup>4-</sup>, MoO<sub>4</sub><sup>2-</sup>) on silver and copper electrodes.<sup>6</sup> In addition, Pettinger has observed SERS for the Au/pyridine system.<sup>7</sup> In all of the above systems, the laser excitation wavelengths used to obtain the SERS spectra were far from resonance with an electronic transition localized in the adsorbate. If, on the other hand, the laser excitation wavelength is coincident with an absorption band in the adsorbate, the resonance Raman (RR) and SER enhancements are multiplicative. Jeanmaire and Van Duyne<sup>2,3</sup> were the first to exploit the enormous enhancement possible under these circumstances when they obtained the combined RR and SER spectrum of crystal violet on both a silver thin film and a bulk polycrystalline electrode using only a few milliwatts of laser power. Since then, however, there have been relatively few adsorbates studied which exhibit this type of combined enhancement.<sup>8</sup>

Although the mechanism of the SERS enhancement is not yet completely understood, much progress has been made toward the development of such understanding.<sup>9</sup> One of our research goals has been to pursue the practical applications of the SERS effect which are independent of its mechanism in parallel with studies directed at the origin of the enhancement. In the biological area, there are numerous possible applications of a practical nature which can be approached with SERS + RRS. One example is to utilize the enhanced sensitivity to determine the Raman or RR spectrum of scarce materials. A second possibility is to use SERS to monitor electron-transfer reactions of redox-active proteins or membrane preparations adsorbed on an electrode. Spontaneous protein adsorption at electrodes, an annoyance in the past, should prove advantageous for this purpose. In the results reported here,

(6) Allen, C. S.; Van Duyne, R. P. *Surf. Sci.*, to be submitted.

(7) Pettinger, B.; Wenning, U.; Wetzel, H. *J. Chem. Phys. Lett.* **1980**, *70*, 49-54.

(8) (a) Hagen, G.; Simic-Glavaski, B.; Yeager, E. *J. Electroanal. Chem.* **1978**, *88*, 269-275. (b) Kotz, R.; Yeager, E. *Ibid.*, submitted.

(9) (a) Furtak, T. E.; Reyes, J. *Surf. Sci.* **1980**, *93*, 351-382. (b) Weber, W. H.; Ford, G. W. *Phys. Rev. Lett.* **1980**, *26*, 1774-1777. (c) Gersten, J.; Nitzan, A. *J. Chem. Phys.* **1980**, *73*, 3023-3037. (d) Otto, A.; Timper, J.; Billmann, J.; Kovacs, G.; Pockrand, I. *Surf. Sci.* **1980**, *92*, L55-L57. (e) Otto, A. *Surf. Sci.* **1980**, *92*, 145-152. (f) Gersten, J. I. *J. Chem. Phys.* **1980**, *72*, 5779-5780. (g) *Ibid.* **1980**, *72*, 5780-5781. (h) Efrima, S.; Metiu, H. *Surf. Sci.* **1980**, *92*, 417-432.