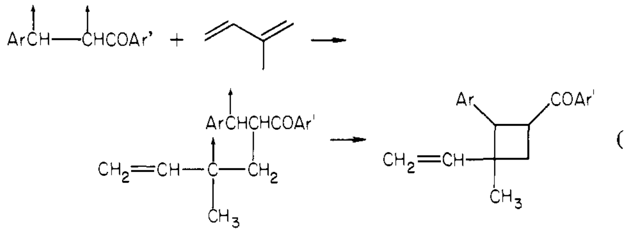
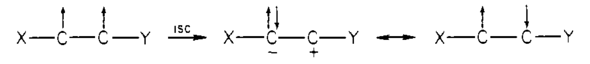
and of the CT or TICT[14,15] type). Increased planarity is always associated with a longer triplet lifetime for an olefin,[8,12,16] and the present cases are even somewhat shorter than the styrenes for which a twisted structure is generally accepted.[8,9] They may be compared to the lifetime of cyclohexenone triplet (30 ns).[2c,6a] Second, the quenching by isoprene, which is largely or wholly chemical and affords predominantly cycloadducts best rationalized as involving the most stable allylic/benzylic biradical (eq 1) is



(1)

nearly unaffected in rate by a polar para substitutent (Table II). This suggests attack on the isoprene by a "benzoylmethylene" terminus largely unaffected by conjugation with the polar substituent, a situation best rationalized by the orthogonal structure of the figure. Third, there is a profound bathochromic shift in the T–T absorption (Table I) as the ability to support charge transfer by polar substituent increases. This requires that the lower triplet be less affected by CT than the upper. We therefore suggest that the lowest triplet is probably largely unaffected by CT, as would be expected for the twisted triplet. It seems safe to conclude that the lifetimes in Table I pertain to the twisted structure, with the probable exception of *p*-(dimethylamino)chalcone. Previous studies[11,17] of stilbene triplets bearing polar substituents have been complicated by planar–twisted equilibria.

The present study is the first in which the effect of polar substituent on intersystem crossing at the twisted geometry is dominant. As can be seen from Table I, that effect is nearly nonexistent. Salem and Rowland[4] include twisted ethylene in their discussion of intersystem crossing in diradicals. They further point out that spin–orbit coupling will in general be proportional to the degree of ionic character in the singlet wave function. We expect that this would be enhanced by substituents X or Y that enhance the ionic resonance form of the singlet below.



$$X{-}\overset{\uparrow}{C}{-}\overset{\uparrow}{C}{-}Y \xrightarrow{\text{isc}} X{-}\underset{-}{\overset{\uparrow\downarrow}{C}}{-}\underset{+}{C}{-}Y \longleftrightarrow X{-}\overset{\uparrow}{C}{-}\overset{\downarrow}{C}{-}Y$$

These considerations would suggest a faster isc rate and thus a shorter lifetime for the cases with a higher ionic contribution in the (twisted) ground singlet. The carbonyl-bearing terminus is clearly the electron-deficient one. The shortest lifetime would thus have been expected for the compounds with donor groups in the para position. In fact, the *p*-$Me_2N$ and *p*-MeO compounds show the longest lifetimes, probably as the result of a planar contribution that dominates for the former and is moderate for the latter. While one might ascribe the decrease in lifetime in the series *p*-CN > *m*-MeO, *p*-Cl > H to the anticipated polar effect, the lifetime decrease in this series is only some 35% in either solvent.

A heavy-atom effect can clearly be observed for *p*-bromochalcone, consistent with substantial spin density at the para position of the chalcone triplet. Neither *m*-Br nor *p'*-Br shows a significant effect, consistent with low spin density in the triplet at these positions.

The results provide at best scant support for the analysis of polar effects on olefin triplet lifetimes by the treatment of Salem and Rowland.[4] We have previously[8,18] anticipated that nuclear motions, which were not considered by Salem and Rowland, may be important.[19]

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**Registry No.** *p*-(Dimethylamino)chalcone, 1030-27-9; *p*-methoxychalcone, 959-33-1; *p*-methylchalcone, 4224-87-7; chalcone, 94-41-7; *p*-chlorochalcone, 956-04-7; *p*-bromochalcone, 1774-66-9; *p*-cyanochalcone, 5724-55-0; *m*-bromochalcone, 29816-74-8; *m*-methoxychalcone, 5470-91-7; *p'*-methoxychalcone, 959-23-9; *p'*-bromochalcone, 2403-27-2; *p'*-cyanochalcone, 31083-73-5; isoprene, 78-79-5.

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[14] Grabowski, Z. R.; Rotkiewicz, K.; Rubaszewska, W.; Kirkor-Kaminska, E. *Acta. Phys. Pol. A* **1978**, *A54*, 767.

[15] Grabowski, Z. R., Rotkiewicz, K.; Siemiarczuk, A., *J. Lumin.*, **1979**, *18/19*, 420.

[16] Stilbene triplets constrained by rigid glasses from twisting can have lifetimes increased over fluid solution lifetimes by many orders of magnitude. In addition to ref 11; see: Heinrich, G.; Blume, H.; and Schulte-Frohlinde, D. *Tetrahedron Lett.* **1967**, 4693. Saltiel, J.; Khalil, G.-E.; and Schanze, K. *Chem. Phys. Lett.* **1980**, *70*, 233.

[17] Bent, D. V.; Schulte-Frohlinde, D. *J. Phys. Chem.* **1974**, *78*, 451–454.

[18] Caldwell, R. A.; Cao, C. V. *J. Am. Chem. Soc.* **1981**, *103*, 3594–3595.

[19] Shaik, S.; Epiotis, N. D. *J. Am. Chem. Soc.* **1978**, *100*, 18. Shaik, S. *Ibid.* **1979**, *101*, 2736, 3184.

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## Azo Precursors to a Putative Biradical in Arene Meta Photoadditions: Evidence for a Novel Concerted Nitrogen Expulsion

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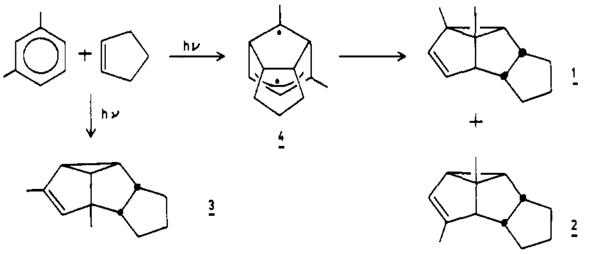
Cyclic azo compounds or 1,2-diazenes have become popular as precursors to organic biradicals.[2] The mechanisms of nitrogen loss in these molecules, however, are not well understood. In particular, subtle questions of concerted vs. stepwise decomposition have proved challenging to experimentalists and theoreticians.[2] We now wish to report a novel concerted nitrogen elimination reaction in two azo compounds corresponding to a retrohomo-Diels–Alder reaction.

Irradiation (254 nm) of an equivolume mixture of *m*-xylene and cyclopentene gave predominantly three products: the endo meta photoadducts **1** and **2**, which have been previously described,[3] and a compound to which we tentatively assign the structure **3**,[4]



which has not been reported. Biradicals such as **4** have been suggested as possible intermediates in arene–olefin photoadditions.[5] To explore this possibility we sought to generate **4** independently.

Reaction of **1** (from preparative GC) with 3-methyltriazoline-2,4-dione (MTAD) gave two major products, **5** (21%) and **6** (49%),[6] which were separated by flash chromatography.

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[1] Recipient of a Camille and Henry Dreyfus Foundation Grant for Newly Appointed Young Faculty in Chemistry.

[2] Engel, P. S. *Chem. Rev.* **1980**, *80*, 99.

[3] Cornelisse, J.; Merritt, V. Y.; Srinivasan, R. *J. Am. Chem. Soc.* **1973**, *95*, 6197.

[4] Tentative assignment based on $^1H$ NMR.

[5] Sheridan, R. S. *Tetrahedron Lett.* **1982**, *23*, 267. Gilbert, A. *Pure Appl. Chem.* **1980**, *23*, 2669 and references cited therein.

[6] Structural assignment is based on $^1H$ NMR, IR, and exact mass spectra; see supplementary material for data.

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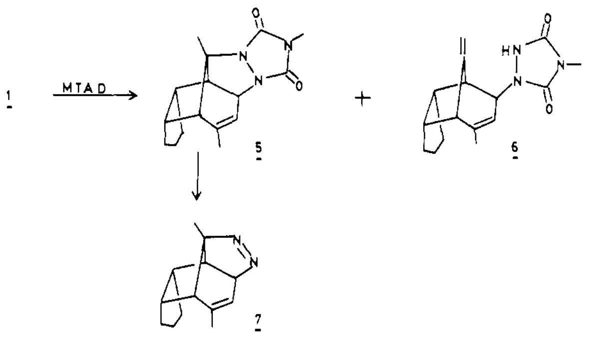
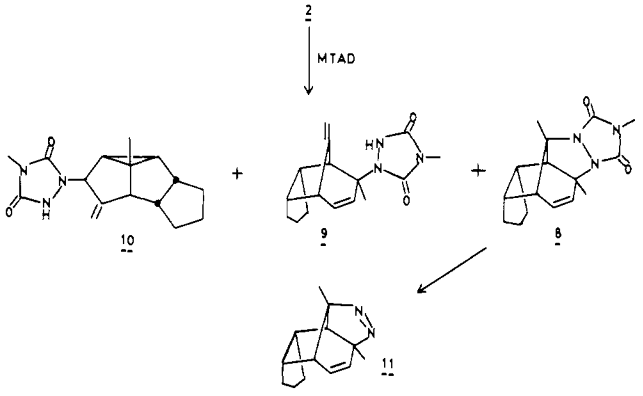
The two products likely arise from electrophilic addition of MTAD to the strained double bond of **1**, followed by rearrangement of the resultant zwitterion.[7,8] The formation of **5** parallels the known addition of other electrophiles to arene meta photoadducts.[9] Hydrolysis and oxidation[10] of **5** gave the azo compound **7** in 44% yield.[6]

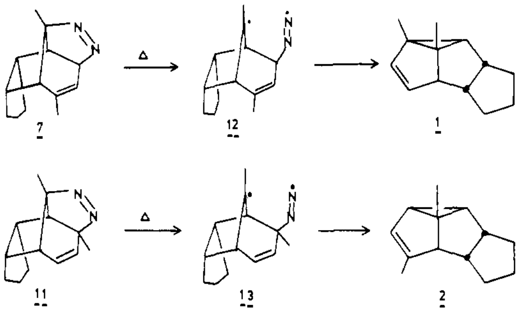


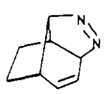
The isomeric adduct **2** unfortunately could not be separated from **3** by preparative GC. Heating pure **1** in the gas phase (12 h, 200 °C) gave a ca. 1:1 mixture of **1** and **2** via vinylcyclopropane equilibration. Preparative GC of this mixture afforded pure **2**. Reaction of **2** with MTAD gave a more complicated mixture of products including **8**,[6] **9**,[4] and ene product **10**.[6] Hydrolysis and oxidation of **8**,[10] obtained in 14% yield by preparative thin-layer chromatography, gave azo compound **11** (53% from **8**).[6]



Thermal decompositions of **7** and **11** were expected to provide two independent routes to biradical **4**. Surprisingly this turned out not to be the case. Thermolysis of **7** (80 °C in benzene-$d_6$) cleanly gave a mixture of **1** and **2** in the ratio of **1**:**2** = 9:1 (by $^1$H NMR). In contrast, thermolysis of the alternate isomer **11** (80 °C in benzene-$d_6$) gave a ratio of 1:2 = 1:9. No other products were observed by GC or $^1$H NMR, and control experiments showed the products to be stable under these conditions.

The difference in product ratios from the two isomeric azo compounds is striking. These results rule out common intermediacy of biradical **4** for the major pathway of decomposition and suggest the involvement of $N_2$ in the product-determining step. Memory effects of this nature have been observed before in the decomposition of azo compounds.[2] Stepwise cleavage followed by reaction of the resulting diazenyl biradicals has been invoked to explain several unusual azo reactions.[11,12] Comparison to other systems suggests that the allylic C–N bond in **7** or **11** would be weaker than the alternate C–N bond by ca. 10 kcal/mol.[2,13] Initial cleavage of this bond can be excluded, however, since a common diazenyl biradical from **7** and **11** would result, leading to identical product ratios. Alternatively, initial cleavage of the nonallylic C–N bonds in **7** and **11** would give the diazenyl biradicals **12** and **13**, respectively. Internal $S_H2'$ displacement would give the observed predominant products. This mechanism, however, is not consistent with the observed kinetics. The azo compounds **7** and **11** readily lose nitrogen at 65 °C ($\tau_{1/2}$ = 26 min for **7** and $\tau_{1/2}$ = 41 min for **11**). This is in line with the decomposition rate of $\tau_{1/2}$ = 15 h at 90 °C reported for **14**.[14] The saturated analogue **15**, in contrast, decomposes only above 250 °C.[14] These results clearly indicate that the C=C double bond is involved in the nitrogen expulsion.

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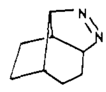
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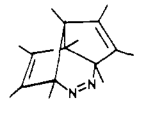
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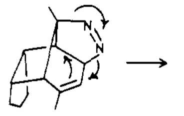
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We therefore suggest that the major product from each azo compound **7** and **11** results primarily from concerted [$\sigma^2s + \sigma^2s + \pi^2s$][15] cycloreversion, as shown above for **7**. Interestingly, stepwise nitrogen loss closely competes with this process and provides a pathway to the alternate regioisomers. Denitrogenations in concert with carbon–carbon bond cleavage are well established in a number of azo compounds.[7,16] At one extreme, 1,2-diazacyclohexa-1,4-dienes cannot be isolated due to extremely facile retro-Diels–Alder reactions. Replacement of the back double bond in these systems by a σ-bond leads to varying degrees of concerted ring fragmentation depending on the strain of the back-bond. Dervan and co-workers have shown that even in monocyclic tetrahydropyridazines, biradical and concerted pathways compete.[17] On the other hand, there is remarkably little precedent for concerted retrohomo-Diels–Alder reactions such as observed here. Borden[18] and Askani[19] have suggested a similar concerted cycloreversion in the octamethylazo compound **16** to rationalize an extremely rapid $N_2$ loss. In this case, however, **16** could not be observed at −30 °C, although it was a logical intermediate from the oxidation of the corresponding hydrazine.[18-20]

In conclusion, these results underscore the point that caution must be exercised in assuming biradicals as intermediates in azo compound deazatizations. Further work is in progress to explore

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[7] Adam, W.; DeLucchi, O. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 762.

[8] The homo-Diels–Alder addition of *N*-phenyl-1,3,5-triazoline-2,4-dione to the meta photoadduct of anisole with cyclopentene has been reported by: Subrahmanyam, G. *Indian J. Chem., Sect. B* **1976**, *14B*, 365.

[9] Ors, J. A.; Srinivasan, R. *J. Org. Chem.* **1977**, *42*, 1321.

[10] Adam, W.; DeLucchi, O.; Erden, I. *J. Am. Chem. Soc.* **1980**, *102*, 4806.

[11] Roth, W. R.; Martin, M. *Liebig Ann. Chem.* **1967**, *702*, 1.

[12] White, D. H.; Condit, P. B.; Bergman, R. G. *J. Am. Chem. Soc.* **1972**, *94*, 7931.

[13] Crawford, A. J.; Ohno, M. *Can. J. Chem*, **1974**, *52*, 3134.

[14] Askani, R.; Hornykiewytoch, T.; Schwertfeger, W.; Jansen, M. *Chem. Ber.* **1980**, *113*, 2154. The greater lability of **7** and **11** compared to **14** is consistent with an activation energy difference of ca. 4 kcal/mol. This is on the order of the effect of methyl substitution observed in other azo compounds.[2]

[15] Woodward, R. B.; Hoffmann, R. "The Conservation of Orbital Symmetry"; Verlag Chemie: Weinheim/Bergstr., Germany, 1971.

[16] Berson, J. A.; Olin, S. S.; Petrillo, E. W., Jr.; Bickart, P. *Tetrahedron* **1974**, *30*, 1639.

[17] Dervan, P. B.; Yuehara, T.; Santilli, D. S. *J. Am. Chem. Soc.* **1979**, *101*, 2069. Dervan, P. B.; Santilli, D. S. *Ibid.* **1980**, *102*, 3862.

[18] Toong, Y. C.; Borden, W. T.; Gold, A. *Tetrahedron Lett.* **1975**, 1549.

[19] Askani, R.; Wieduwilt, M. *Chem. Ber.* **1976**, *109*, 1887.

[20] The clean generation of only the ring-closure products[7,21] indicates that dipolar cycloreversion to diazo compounds is not occurring in **7** and **11**. Moreover, no equilibration of **7** and **11** was observed on partial thermal decomposition.

[21] See, for example: Kumagai, T.; Ohba, Y.; Mukai, T. *Tetrahedron Lett.* **1982**, *23*, 439.

the generality of these cycloreversions. The photochemistry of **7** and **11** will be reported in a separate publication.

**Acknowledgment.** We thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, the Camille and Henry Dreyfus Foundation, and the National Science Foundation for support of this work.

**Supplementary Material Available:** Spectral data for **3**, **5**, **7**, **8**, **10**, and **11** (1 page). Ordering information is given on any current masthead page.

# Conductivity Measurement of an X-ray Absorption Spectrum: Re $L_{III}$ Near-Edge Structure of $Re_2(CO)_{10}$ in 2,2,4-Trimethylpentane

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We report in this communication the first measurements of an X-ray absorption spectrum by means of X-ray photoconductivity in a hydrocarbon solution. $Re_2(CO)_{10}$ in 2,2,4-trimethylpentane has been used for these measurments. The main objective of this report is to demonstrate the feasibility of this technique and its potential applications.

Recent advances in synchroton radiation technology[1] have greatly facilitated the development of X-ray absorption spectrometry. Aside from direct absorption measurements in the transmission mode, various techniques such as electron yield,[2,3] ion yield,[4,5] and fluorescence yield[6-9] have been developed for special situations where high sensitivity is needed and the transmission measurement is not applicable. Of all these techniques, the basic assumption is that the yield is proportional to the absorption cross section. It has been demonstrated[2-9] that the assumption is generally valid particularly in the EXAFS portion of the spectrum, although precise agreement of the EXAFS amplitude is not always obtained.[10]

The technique we introduce here is the measurement of photoconductivity of a solution. The electrons and ions formed as a result of a photon absorption process are collected by an electric field applied across the solution. The signal in such an experiment can be written

$$I_1/I_0 = K(E)(1 - e^{-\mu t}) \qquad (1)$$

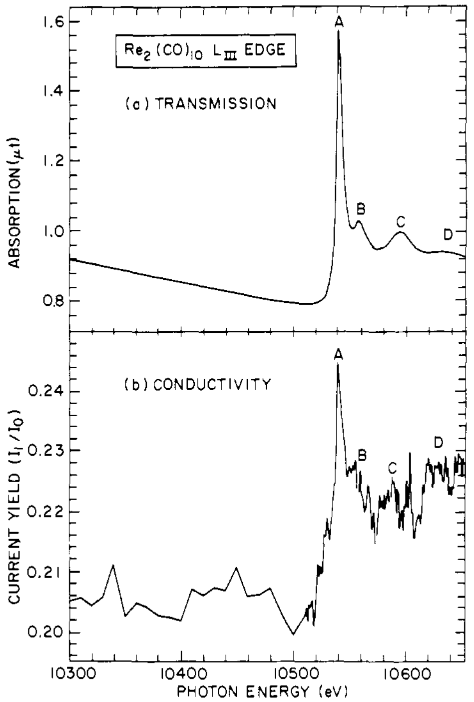

**Figure 1.** Re $L_{III}$ near-edge structure of $Re_2(CO)_{10}$ in 2,2,4-trimethylpentane obtained by (a) transmission measurement and (b) conductivity measurement. The transmission measurement has been calibrated to give the actual $\mu t$ of the solution. The current measurement is simply a plot of $I_1/I_0$, which is not necessarily equal to $\mu t$ (see text).

where $I_1$ and $I_0$ are the photocurrent and incident photon signals, respectively, $\mu$ is the total sample absorption, and $t$ is the sample thickness. $K(E)$ is the proportionality constant ($E$ being the photon energy) relating the absorption to the photoinduced current. The current comes about from photoionization and cascade processes involving the excited photoelectron and the decay of the core hole by Auger and fluorescent processes.[11,12] It is not our purpose here to make a detailed study of $K(E)$, but rather to point out some general features. Below the edge, as the photon energy is increased there is more energy available for current production, and thus, $K(E)$ should slowly increase with energy. At the $L_{III}$ absorption threshold, however, the $2_{p_{3/2}}$ core hole is created. This core hole can decay either via an Auger process or by emission of a fluorescence photon. While the Auger electrons can generate a lot of secondary charges, the fluorescence photon has a finite probability of escaping the sample, resulting in no current. In the present case the probability of fluorescence is small, and therefore we expect $K(E)$ to be a function of energy with possibly a small decrease at the edge. It must be pointed out that $K(E)$ includes the collection efficiency of the cell. This is affected primarily by recombination of the electrons and ions before they reach the collection plates. This process is more likely as the absorption is increased and also would decrease $K(E)$ as the absorption increases through the edge.

The measurements were made at CHESS (Cornell High Energy Synchroton Source). A channel-cut Si(220) crystal monochrometer was used. The horizontal slit was closed down to ~0.2 mm to achieve high resolution. The experimental arrangement involves the use of solution cells made of quartz (5-mm i.d., 5 mm thick) and equipped with two Al-coated Mylar windows. The windows were used as electrodes. The cell was placed in a metal container that is positioned in place of the sample holder used in transmission measurements.[1] Ion chambers were used to measure

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(1) See, for example: "Synchrotron Radiation Research", H. Winick and S. Doniach, Eds., Plenum 1980.

(2) P. H. Citrin, P. Eisenberger, and R. C. Hewitt, *Phys. Rev. Lett.*, **41**, 309 (1978); **45**, 1948 (1980).

(3) J. Stöhr, L. Johansson, I. Lindau, and P. Pianetta, *Phys. Rev. B*, **20**, 664 (1979).

(4) M. L. Knotek and P. J. Feibelman, *Phys. Rev. Lett.*, **40**, 964 (1978).

(5) R. Jaeger, J. Feldhans, J. Haase, J. Stöhr, Z. Hussain, D. Menzel, and D. Norman, *Phys. Rev. Lett.*, **45**, 1870 (1980).

(6) J. Jaklevic, J. A. Kirby, M. P. Klein, A. S. Robertson, G. S. Brown, and P. Eisenberger, *Solid State Commun.* **23**, 679 (1977).

(7) E. A. Stern and S. M. Heald, *Rev. Sci. Instrum.* **50**, 1579 (1979).

(8) J. Hastings, P. Eisenberger, B. Lengeler, and M. L. Perlman, *Phys. Rev. Lett.*, **43**, 1807 (1979).

(9) R. G. Shulman, P. Eisenberger, B. K. Teo, B. M. Kincaid, and G. S. Brown, *J. Mol. Biol.*, **124**, 305 (1978).

(10) G. Martens, P. Rabe, N. Schwentner, and A. Werner, *J. Phys. C*, **11**, 3125 (1978).

(11) K. Siegbahn, C. Nordling, A. Fahlman, R. Nordberg, K. Homrin, J. Hedman, G. Johansson, T. Bergmark, S. E. Karlsson, I. Lindgren, and B. Lindberg, "ESCA", Atomic Molecular and Solid State Structure Studied by means of Electron Sepectroscopy, Nova Acta Reginal Soc. Sci., Upsaliensis (IV), Vol. 20, 1967.

(12) R. W. Fink, R. C. Jopson, Hans Mark, and C. D. Swift, *Rev. Mod. Phys.*, **38**, 513 (1966).

0002-7863/83/1505-5142$01.50/0