## Photo Conductivity of Liquid Tetramethylsilane

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Intrinsic photo conductivity of liquid tetramethylsilane was observed in the wave length region from 1100 to 1500 Å. The photo ionization threshold $E_L$ has been determined to be $E_L = 8.1$ eV.

Very few investigations have been carried out so far on the direct photo ionization of non-polar liquids. Vermeil et al. [1] detected an increase of conductivity in some liquid hydrocarbons when subjected to the light of rare gas resonance lamps. Recently similar experiments were performed by Casanovas and co-workers at the University of Toulouse [2, 3]. It was estimated that the ionization threshold energy of the molecules in the gas phase is reduced for the corresponding liquids by 0.5 eV to 1 eV.

Direct measurements of the ionization threshold energy for liquid xenon were reported by Roberts and Wilson [4], Asaf and Steinberger [5] and Spear and LeComber [6]. While Roberts and Wilson found a strong increase of the photo current with photon energy above 8.9 eV, Asaf and Steinberger determined the threshold energy to 9.2 eV, which agrees with the value reported by Spear and LeComber.

The photo ionization threshold in the liquid phase $E_L$ should be given by

$$E_L = E_G + V_0 + P_+ \tag{1}$$

with $E_G$ the gas phase energy, $P_+$ the polarization energy of the positive ion and $V_0$ the electron affinity of the liquid.

The electron affinity or the energy of the electronic conduction level has been determined for many hydrocarbons and liquefied rare gases by means of the photoelectric effect on a metal electrode [7–9]. The polarization energy of the positive ion can then be obtained if $E_L$ is measured.

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On the other hand, $P_+$ can be estimated from Born's equation [10] which yields for an ion of radius $r$

$$P = -\frac{e^2}{2r}\left(1 - \frac{1}{\varepsilon}\right) \tag{2}$$

with $\varepsilon$ the relative dielectric constant of the liquid and $e$ the elementary charge.

Here we wish to report the results of photoconductivity experiments on liquid tetramethylsilane ($(CH_3)_4Si$) at 22 °C. The liquid was contained in a parallel plate conductivity cell with 2 mm plate separation. One electrode consisted of a thin gold layer (thickness approximately 150 Å) evaporated on to a LiF plate which served as the entrance window for the radiation. The counter electrode was made of gold plated brass, the cell body was of stainless steel. Synchrotron radiation from the storage ring DORIS was monochromatized by a high intensity monochromator [11]. The resolution was adjusted to approximately 0.1 eV. With DORIS operating in the single bunch mode (10–20 mA current of circulating electrons) an intensity of about $10^{10}$ photons/sec was available at the entrance window of the conductivity cell. In the multi mode (200–400 mA current) the intensity would be increased at least by a factor of 10. DC-voltages up to 3 kV were applied across the liquid gap and the photocurrents were measured with a Keithley Mod 602 electrometer. At a particular voltage the wavelength of the radiation was scanned from 1100 Å to 1600 Å and the photo current was recorded. Depending on the applied voltage the photo current exceeded the dark currents by a factor of up to 4. The dark currents were subtracted from the currents under illumination in order to obtain the photo currents. Figure 1 a shows a typical photo conductivity spectrum obtained. Data were recorded for different polarities and voltages. The spectral dependence of the incident intensity, and the transmission of the cell window and the gold electrode were determined by observing the luminescence intensity of sodium salicylate placed behind the gold film (Figure 1 b). In Fig. 1 c the corrected photo current as a function of wavelength is shown. The current begins to rise below 1500 Å and a second steep rise is observed below 1150 Å.

Since the intensity of the synchrotron radiation decreased with time, photo conductivity spectra taken at different times were normalized according

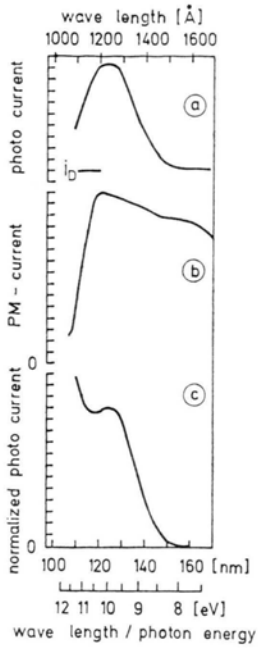


Fig. 1. a) Observed photo current as a function of wave length for liquid Tetramethylsilane; applied voltage 1300 V, $i_D = 5.5$ pA, maximum photo current $i_{max} = 19.5$ pA. b) Efficiency of the monochromator and transmission of LiF-window and gold layer measured as the photo current of a photomultiplier produced by the luminescence of sodium salicylate. c) Photo current per incident photon, corrected data of Fig. 1a (see text).

to the magnitude of the electron current in the storage ring.

In order to determine the threshold $E_L$, the photo conductivity $\sigma$ in arbitrary units as a function of photon energy was plotted and a power function was fitted to the points. A surprisingly good fit was obtained with

$$\sigma \propto (E - E_L)^{3/2} \quad (3)$$

and $E_L = 8.1$ eV (Figure 2). For the gas phase ionization energy Jonas et al. [12] reported $E_G = 9.79$ eV. $V_0$ was determined by Holroyd et al. and the mean of the values reported by them is $V_0 = -0.57$ eV [7, 8, 13]. From Eq. (1) $P_+ = -1.12$ eV is obtained, which yields an ionic radius of $r = 2.95$ Å comparable to the hard core radius of the molecule.

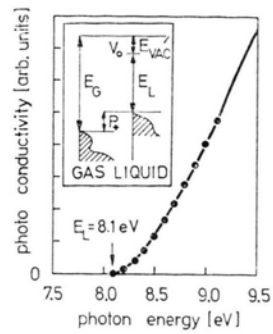


Fig. 2. Computer averaged dependence of photo conductivity on photon energy for liquid Tetramethylsilane (this plot contains 11 photo conductivity spectra for different voltage and intensities). The points have been calculated according to Equation (3). In the insert a schematic energy level diagram for gaseous and liquid Tetramethylsilane is shown.

The second threshold observed in liquid tetramethylsilane at around 10.75 eV may be compared with the rise in the photo electron spectrum from the gas at 12.2 eV. The difference is 1.45 eV as compared to 1.65 eV for the first threshold. This discrepancy may be due to the fact that the second threshold in the liquid could not be determined from the data in the same way as the first threshold. The photo current due to the second ionization process still contains a considerable contribution due to the first ionization, which impedes the exact determination of this threshold.

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## Eine PMO-theoretische Untersuchung der benzogenen Diels-Alder-Reaktion polycyclischer aromatischer Kohlenwasserstoffe

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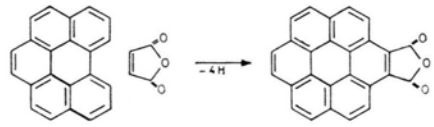
*A PMO-theoretical Treatment of the Benzogenic Diels-Alder Reaction of Polycyclic Aromatic Hydrocarbons*

Experimental reaction rates of the benzogenic Diels-Alder reaction of polycyclic aromatic hydrocarbons with maleic anhydride are correlated with the corresponding bislocalization energies calculated by the PMO method. The observed relations between the localization energies of the reacting centres and the topology of the hydrocarbons can be qualitatively understood on the basis of Clar's $\pi$-sextet model of polycyclic systems and Polansky's pars orbital method.

Wie Benzo[ghi]perylen (I) reagieren zahlreiche polycyclische aromatische Kohlenwasserstoffe (PAK), die eine periphere cisoide $C_4$-Anordnung enthalten, mit Maleinsäureanhydrid bei Anwesenheit eines geeigneten Dehydrierungsmittels zu vollaromatischen Dicarbonsäureanhydriden II („Benzogene Diels-Alder-Reaktion") [1]:




I II

Der geschwindigkeitsbestimmende Schritt der benzogenen Diels-Alder-Reaktion ist die primäre Bildung des Diels-Alder-Addukts [2], dessen Isolierung in einigen Fällen (bei Abwesenheit eines Dehydrierungsmittels) gelingt [3, 4].

Vor längerem wurden die unter völlig gleichen Bedingungen gemessenen relativen Reaktionsgeschwindigkeiten $(RG)_{rel}$ (bezogen auf Benzo[ghi]perylen) der benzogenen Diels-Alder-Reaktion der in Abb. 1 aufgeführten PAK mitgeteilt (Dehydrie-

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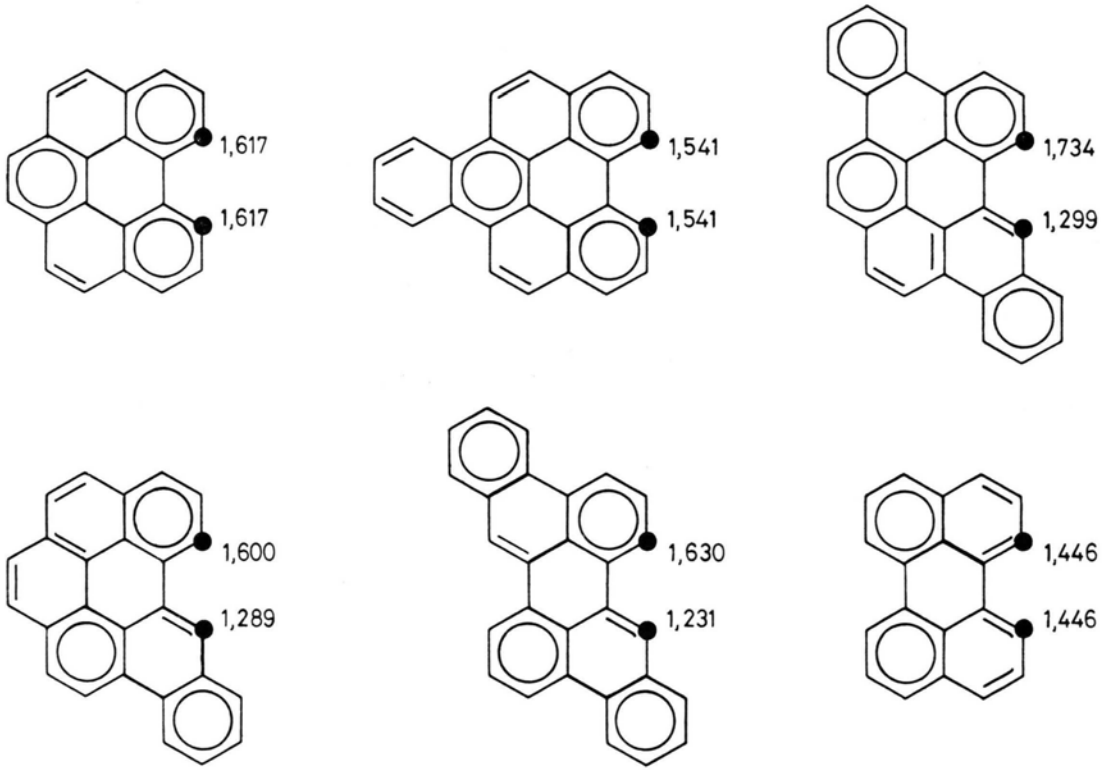



Abb. 1. Lokalisierungsenergien (x $\beta^{-1}$) (ber. mit der PMO-Methode) für die in der benzogenen Diels-Alder-Reaktion reagierenden Zentren einiger polycyclischer aromatischer Kohlenwasserstoffe der Perylen-Reihe.

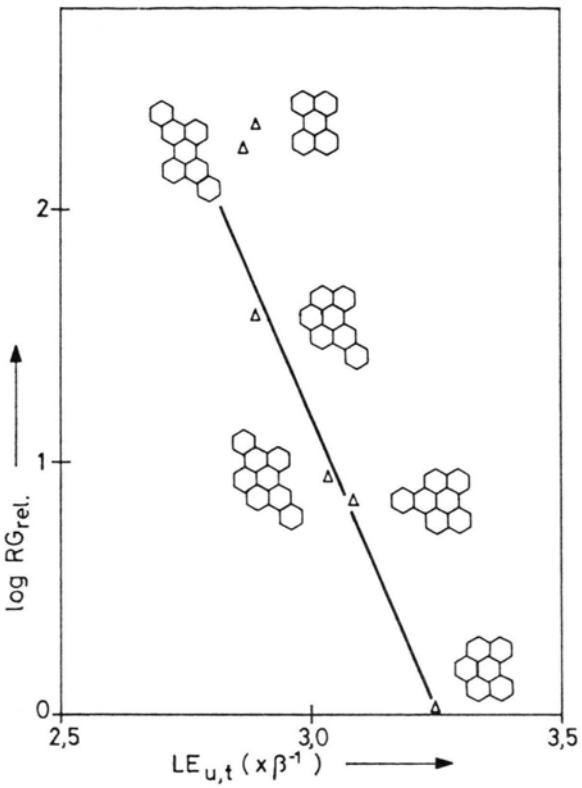


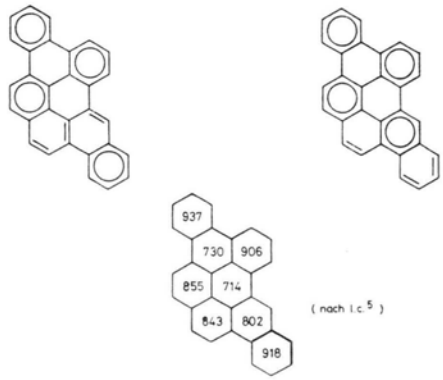

Abb. 2. Zusammenhang zwischen log $(RG)_{rel}$ der benzogenen Diels-Alder-Reaktion und Bislokalisierungsenergien (x $\beta^{-1}$) der reagierenden Zentren.

rungsmittel: Chloranil) [2]. Die log $(RG)_{rel}$ sind linear korreliert mit den nach der Polanskyschen Pars-orbital-Methode [5] berechneten Charakterordnungen der reagierenden butadienoiden Zonen [2].

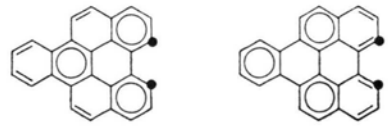
Es wurden jetzt für die Kohlenwasserstoffe die an den Formeln angegebenen Lokalisierungsenergien (x $\beta^{-1}$) der reagierenden Zentren nach der Methode von Dewar [6] berechnet (Abbildung 1). Die Bislokalisierungsenergien geben eine lineare Korrelation mit den log $(RG)_{rel}$ der benzogenen Diels-Alder-Reaktion (Abbildung 2) [7].

Zum qualitativen Verständnis der Beziehungen zwischen den berechneten Lokalisierungsenergien und der Topologie der Systeme sind Clar's $\pi$-Sextett-Modell von PAK [3, 4] und das Pars-orbital-Konzept [5] geeignet:

1. Bei Systemen mit unterschiedlicher Lokalisierungsenergie an den beiden reagierenden Zentren wird die größere Lokalisierungsenergie stets an dem Zentrum gefunden, das zu einer benzoiden Teilstruktur gehört, die kleinere Lokalisierungsenergie stets am Zentrum, das zu einer äthylenoiden Teilstruktur gehört, in Übereinstimmung damit, daß die Lokalisierungsenergie des Benzols größer ist als die des Äthylens. Für die Betrachtung bilden die mit der Pars-orbital-Methode berechneten benzoiden Charakterordnungen eine vorteilhaftere Basis als Clar's Formeln mit der maximalen Zahl an inhärenten $\pi$-Sextetten, da es in vielen Fällen für einen PAK mehrere Clar-Formeln mit gleicher Zahl von inhärenten $\pi$-Sextetten gibt:




2. Bei Systemen, bei denen die an der benzogenen Diels-Alder-Reaktion beteiligten Zentren zu Molekülzonen gehören, die in Clar-Formeln sowohl benzoid wie nicht-benzoid repräsentiert werden können, sind die Lokalisierungsenergien der reagierenden Zentren kleiner als in Systemen in denen die Zentren zu Molekülzonen gehören, die in Clar-Formeln nur benzoid repräsentiert werden können (z.B. Benzo[ghi]perylen(I)), was mit der Zunahme der Lokalisierungsenergien beim Übergang vom Naphthalin zum Benzol korrespondiert.



3. Daß die Lokalisierungsenergien für Zentren in benzoiden Teilstrukturen von PAK kleiner sind als im Benzol (2.31 $\beta$) oder in allbenzoiden PAK [5] wie Triphenylen (2.12 $\beta$ in der 2-Position) steht in Übereinstimmung mit den Beträgen der benzoiden Charakterordnungen [5] der verglichenen Systeme.

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