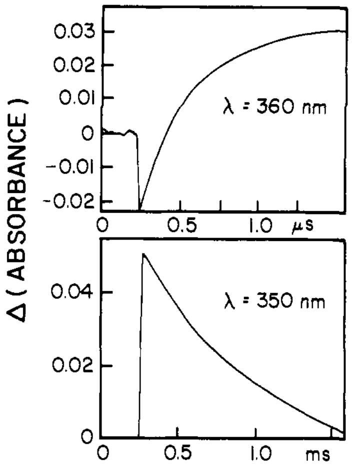


Figure 3. Kinetics of ketene formation from precursor at 360 nm and its slow reaction with water at 350 nm.

pathlength 2 mm) at 337 nm. Two transient spectra were observed. The first one appeared immediately after the laser pulse (Figure 1b, solid line). This differential spectrum changed within 330 ns (rate: $3 \times 10^{6}\ \mathrm{s^{-1}}$) to produce the second spectrum (Figure 1b, dashed line). The kinetics of this transformation were first order and independent of wavelength. An example of the transient kinetics at 360 nm is shown in Figure 3. Furthermore, the transient absorbances are intensity independent; i.e., they are not products of biphotonic chemistry. These results indicate that two distinct intermediates exist, one precursor to the other.

The second intermediate slowly decayed by first-order kinetics (rate: $1.8 \times 10^{3}\ \mathrm{s^{-1}}$), as can be seen at 350 nm in Figure 3. It can clearly be assigned to the ketene since its absorption spectrum and decay kinetics are in good agreement with those reported in the literature.[4] It is known[8,9] that ketenes may undergo three types of reactions shown in Figure 2 (5, 6, and 7). They are respectively reaction with the solvent (reaction 5), ketene–ketene dimerization (reaction 6), and reaction with the parent diazoketone (reaction 7). To determine which of these reactions contributes to the observed decay kinetics both the laser intensity (ketene concentration) and the diazoketone concentration were varied by a factor of 5. No dependences were detectable in our experiments indicating that the observed rate constant is due to reaction of ketene with water (reaction 5, Figure 2). This is in agreement with continuous photolysis results[1,7] where sodium 3-carboxyindene-7-sulfonate is found to be the main product.

The first intermediate could be either a ketocarbene or an oxirene. It has been shown through theoretical studies that ketocarbene and oxirene have similar energies depending on the compound considered.[2,10] However, it is generally concluded that oxirene should be longer lived than ketocarbene because of its larger barrier to ketene formation.[2,10] Another potential test to distinguish between oxirene and ketocarbene is their reactivity toward added reagents. It is known that many carbenes[11] and ketocarbenes[3] will react with O_2; however, the first intermediate was insensitive to oxygen within its 330-ns lifetime. Another common carbene scavenger is methanol which reacts with rate constants typically between 10^{7} and $10^{10}\ \mathrm{M^{-1}\ s^{-1}}$.[12] Thus one would expect that in the presence of high concentrations of methanol that the ketocarbene would be entirely scavenged and ketene and its products would not be observed. This is contrary to the evidence of continuous photolysis.[7] Similarly, no reaction of the first intermediate with methanol (1:1 water–methanol mixture) was observed in this laser photolysis study although the rate of ketene formation was enhanced by a factor of 3. So all of the evidence points to the fact that the first intermediate observed in our experiments is not ketocarbene and, therefore, is most likely oxirene. It is noted that zwitterionic resonance structures of ketocarbene may exist and play a role in polar solvents. however, we would expect the reactivity of these resonance structures with molecular oxygen and methanol to be similar to that of carbene.

The dynamics from the excitation of sodium 1-oxo-2-diazonaphthoquinone-5-sulfonate to the final product can now be discussed. The excited state involved in the Wolff rearrangement is most likely the first excited singlet state since oxirene appears within 10 ns while the singlet state has at most a ns lifetime. This is in agreement with other reports.[3] Ketene is formed from oxirene; however, it probably involves ketocarbene as an undetectable step. Therefore, the rate constant for ketene formation, $3 \times 10^{6}\ \mathrm{s^{-1}}$, can either be assigned to k_4 or k_{-2} in Figure 2 (k_3 being obviously much faster than k_{-2}). Finally the slow disappearance of ketene can be ascribed to its reaction with water (reaction 5 in Figure 2), and its rate constant k_s is $1.8 \times 10^{3}\ \mathrm{s^{-1}}$.

In conclusion, the dynamics of the Wolff rearrangement have been observed in detail by laser spectroscopy in water at room temperature. The primary precursor to a ketene has been spectrally detected, and based on its reactivity it has been assigned to be oxirene. The direct observation of the precursor to ketene and its dynamics opens new possibilities for understanding the Wolff rearrangement and the interrelationship between ketocarbene and oxirene. Further studies on other α-diazoketones in various solvents are in progress.

Acknowledgment. K.T. is grateful to Prof. J. Higuchi and Dr. M. Yagi for their encouraging discussions. We are grateful to Dr. M. Bohorquez for fluorescence lifetime measurements. The research described herein was supported by the Office of Basic Energy Sciences of the Department of Energy. This is document No. NDRL-2973 from the Notre Dame Radiation Laboratory.

Registry No. Sodium 1-oxo-2-diazonaphthoquinone-5-sulfonate, 2657-00-3.

---

(8) Wiberg, K. B.; Hutton, T. W. *J. Am. Chem. Soc.* **1954**, *76*, 5367.

(9) Yates, P.; Robb, E. W. *J. Am. Chem. Soc.* **1957**, *79*, 5760.

(10) Tanaka, K.; Yoshimine, M. *J. Am. Chem. Soc.* **1980**, *102*, 7655.

(11) (a) Casal, H. L.; Tanner, M.; Werstiuk, N. H.; Scaiano, J. C. *J. Am. Chem. Soc.* **1985**, *107*, 4616. (b) Werstiuk, N. H.; Casal, H. L.; Scaiano, J. C. *Can. J. Chem.* **1984**, *62*, 2391.

(12) (a) Griller, D.; Liu, M. T. H.; Montgomery, C. R.; Scaiano, J. C.; Wong, P. C. *J. Org. Chem.* **1983**, *48*, 1359. (b) Griller, D.; Nazran, A. S.; Scaiano, J. C. *J. Am. Chem. Soc.* **1984**, *106*, 198.

A Series of Donor–Acceptor Molecules of the Form $NH_2(C_6H_4)(C{\equiv}C)_n(C_6H_4)NO_2$. Unusual Effects of Varying *n*

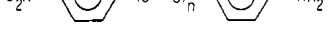
A. E. Stiegman,* Vincent M. Miskowski, Joseph W. Perry, and Daniel R. Coulter

Jet Propulsion Laboratory
California Institute of Technology
Pasadena, California 91109

Received June 8, 1987

We would like to report some interesting spectroscopic results obtained from a newly synthesized series of donor–acceptor diphenylpolyyne molecules.

The compounds reported here are of the form **1**, **2**, and **3**, where



1, 2, 3: n = 1,2,3

the number of acetylenes, *n*, varies from one to three. These compounds provide a basis for investigating charge-transfer excited states as the distance between the donor and acceptor chromophores is systematically varied. Additionally, these compounds are of interest with respect to their potential nonlinear optical

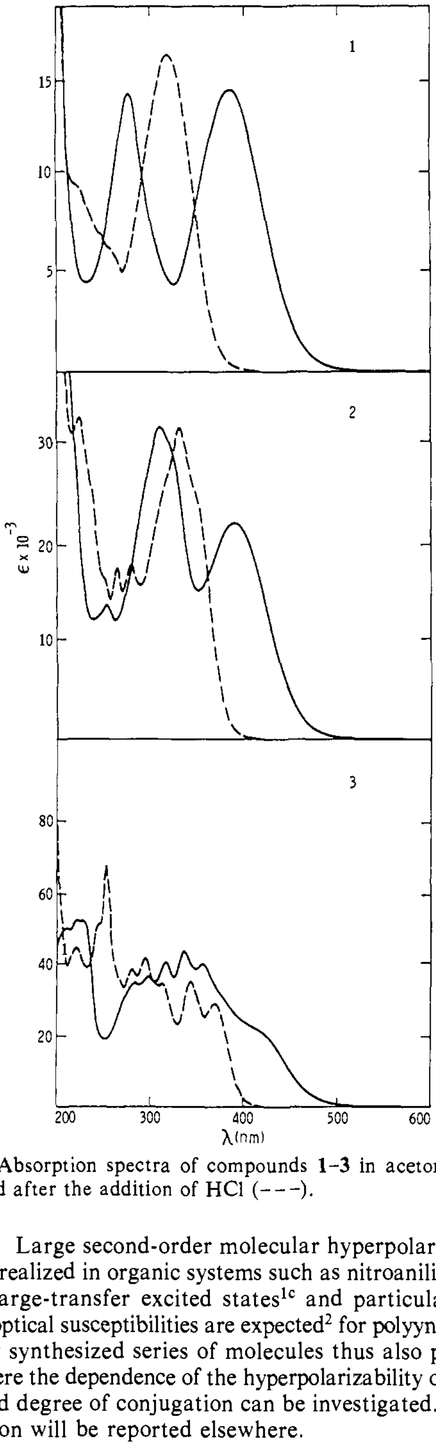


Figure 1. Absorption spectra of compounds **1**–**3** in acetonitrile (—) solution and after the addition of HCl (- - -).

properties. Large second-order molecular hyperpolarizabilities have been realized in organic systems such as nitroanilines which exhibit charge-transfer excited states[1c] and particularly large nonlinear optical susceptibilities are expected[2] for polyyne systems. The newly synthesized series of molecules thus also provides a system where the dependence of the hyperpolarizability on transfer lengths and degree of conjugation can be investigated. Such an investigation will be reported elsewhere.

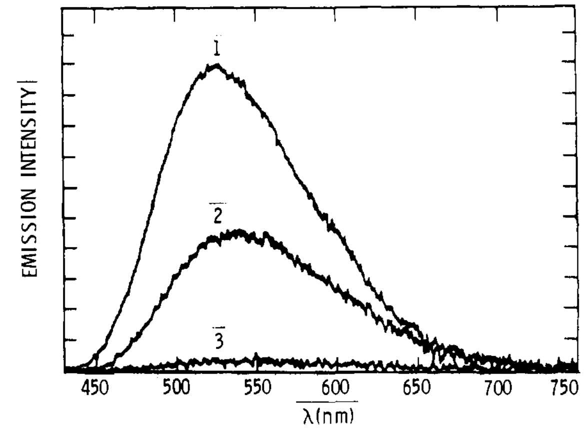


Figure 2. Corrected emission spectra of compounds **1**–**3**. The spectra were measured in toluene solution employing 361-nm excitation, at which wavelength the optical densities of all three samples were matched. The relative intensities reflect the relative quantum yields of the compounds.

Table I

	absorption[a]		emission[b]	
n	λ_{max} (nm)	$\epsilon \times 10^{-3}$	λ_{max} (nm)	Φ[c]
1	384	14	526	0.091
2	385	22	536	0.045
3	410 (sh)	21	543	0.005[d]

[a] In CH_3CN solution. [b] In toluene solution. [c] The quantum yields were measured relative to quinine sulfate in 1 N H_2SO_4 by using 361-nm excitation and were corrected for the different indices of refraction. [d] For 420-nm excitation, the observed value is 0.010. The wavelength dependence is discussed in the text.

While the complete synthetic details will be presented separately, a general outline of the synthesis is as follows. The *p*-amino-*p*′-nitrodiphenylethyne (**1**)[1] was synthesized by the procedure outlined by Hooper[3] which involves the reaction of copper(I) nitrophenylacetylide with *p*-iodoaniline. The *p*-amino-*p*′-nitrodiphenylbutadiyne (**2**) and *p*-amino-*p*′-nitrodiphenylhexatriyne (**3**) were synthesized by coupling *p*-nitrophenylacetylene and *p*-nitrophenylbutadiyne, respectively, with *p*-aminophenylacetylene by means of the Hay catalyst.[4]

The UV-vis absorption spectra of these compounds in dilute solution are shown in Figure 1. Compounds **1** and **2** have similar spectra characterized by a broad intense band with a maximum in the region of 385 nm and extinction coefficients of 1.4×10^4 and 2.2×10^4, respectively. The spectrum of compound **3** is more complicated due to low-energy $\pi \rightarrow \pi^*$ transitions associated with the diphenylhexatriyne framework.[5] However, the broad low-energy peak in compounds **1** and **2** can be seen as a shoulder at 410 nm ($\epsilon = 2.1 \times 10^4$) in compound **3**. This broad peak, which for all three compounds vanishes upon protonation with HCl, is assigned as the intramolecular charge-transfer (ICT) transition emanating from the N lone pair on the amine and terminating in an empty π^* orbital on the nitro group. This transition is absent in either the *p*-nitrophenylacetylene or *p*-aminophenylacetylene precursors and does not appear until both the amino and nitro groups are linked. The energy and intensity of this charge-transfer band is analogous to the well-studied ICT band of *p*-nitroaniline.[6,7] An even more striking comparison is to the molecule 4-amino-4′-nitrobiphenyl which has an ICT band at 375 nm ($\epsilon = 1.6 \times 10^4$).[8]

---

(1) The analogous compound *p*-(dimethylamino)-*p*′-nitrodiphenylethyne has been previously reported. (a) van Koten, G.; ten Hoedt, R. W. M.; Noltes, J. G. *J. Org. Chem.* **1977**, *42*, 2705–2711. (b) Gallagher, M. J.; Noerdin, H. *Aust. J. Chem.* **1985**, *38*, 997–1005. (c) Buckley, A.; Choe, E.; DeMartino, R.; Leslie, T.; Nelson, G.; Stamatoff, J.; Stuetz, D.; Yoon, H. *Polymer Preprints* **1985**, *54*, 502–509.

(2) Beratan, D. N.; Onuchic, J. N.; Perry, J. W. *J. Phys. Chem.* **1987**, *91*, 2696–2698.

(3) Bond, C. C.; Hooper, M. *J. Chem. Soc. C* **1969**, 2453–2460.

(4) (a) Hay, A. S. *J. Org. Chem.* **1962**, *27*, 3320–3321. (b) Eastmond, R., Johnson, T. R.; Walton, D. R. M. *Tetrahedron* **1972**, *28*, 4601–4616.

(5) (a) Kobayashi, M.; Hoshi, T.; Okubo, J.; Hiratsuka, H.; Harazono, T.; Nakagawa, M.; Tanizaki, Y. *Bull. Chem. Soc. Jpn.* **1984**, *57*, 2905–2909. (b) Hoshi, T.; Okubo, J.; Kobayashi, M.; Tanizaki, Y *J. Am. Chem. Soc.* **1986**, *108*, 3867–3872.

(6) (a) Jaffé, H. H.; Orchin, M. *Theory and Applications of Ultraviolet Spectroscopy*; John Wiley: New York, 1962; p 260. (b) Millefiori, S.; Favini, G.; Millefiori, A.; Grasso, D. *Spectrochim Acta* **1977**, *33A*, 21–27. (c) Bertinelli, F.; Palmieri, P.; Brillante, A.; Taliani, C. *Chem. Phys.* **1977**, *25*, 333–341. (d) Khalil, O. S.; Seliskar, C. J.; McGlynn, S. P. *J. Mol. Spectrosc.* **1978**, *70*, 74–83.

(7) Interestingly, these molecules differ from *p*-nitroaniline in that their absorption spectra do not show a significant solvent dependence. However, as discussed in the text, the emission maxima do show a dramatic solvent dependence. The implication of this for the nature of the ICT state is currently under investigation.

(8) Sherwood, D. W.; Calvin, M. *J. Am. Chem. Soc.* **1942**, *64*, 1350–1353.

The high-energy absorption bands are, for all n, largely unaffected by HCl protonation (Figure 1). The spectra of the protonated forms are very similar to those of the diphenylpolyynes, particularly for **3**, reported by Kobayashi et al.[5] and are attributable to $\pi \rightarrow \pi^*$ transitions.

These molecules show a strong emission from the charge-transfer state. The lifetime of the emission is short, less than the response function of our transient emission system (<5 ns), indicating a fluorescence. We have not been able to observe any phosphorescence even at 77 K. The emission maxima are highly solvent sensitive which is typical of emissive charge-transfer states which experience large dipole changes between the ground and the excited state.[9,10] For compound **2** the emission maximum is at 536 nm in toluene and 590 nm in ether.[11] The emission maxima show little change for the series of molecules in a given solvent, and both the emission half width ($\sim$4000 cm^{-1}) and Stokes shift ($\sim$7000 cm^{-1}) are likewise insensitive to n. However, the emission intensity decreases dramatically (Figure 2) in going from compound **1** to **3**. The pertinent spectroscopic data are summarized in Table I.

Corrected excitation spectra of these compounds reproduce the strong ICT band in all cases, but the higher energy features which are associated with $\pi \rightarrow \pi^*$ transitions of the diphenylpolyyne[5] appear to be much weaker than in the absorption spectra. The overlap of $\pi \rightarrow \pi^*$ transitions with the ICT band for **3** results in a strong wavelength dependence of the emission quantum yield for that molecule.

Taken as a whole the spectroscopic data suggest several things about the nature of these charge-transfer excited states. The significant observations from this series are the relative invariance in energy and intensity of the ICT band as the distance between the donor and acceptor is varied and the strong dependence of the emission quantum yield on n. The results from absorption spectroscopy indicate that while interaction between the donor and acceptor is efficient, as suggested by the large extinction coefficients, it remains relatively constant as the delocalized π system which connects the D/A pair is lengthened.

To a first approximation the ICT band can be thought of as a weak aniline $n(NH_2) \rightarrow \pi^*$ transition which gains intensity as a result of mixing π^* orbitals with the π^* orbitals on the nitro group.[6] Equivalently, this mixing may be described as a result of coupling an $n\pi^*$ state with a diphenylpolyyne state and a state with a charge-transfer configuration (ICT). Our results indicate that while the delocalized π/π^* orbitals are necessary for communication between the donor and acceptor, large changes in the energy of the diphenylpolyyne $\pi \rightarrow \pi^*$ transitions do not alter greatly the energy and intensity of the ICT electronic transition. This suggests a relatively small amount of mixing of the diphenylpolyyne $\pi\pi^*$ state with the $n\pi^*$ and ICT states. This is reasonable since diphenylpolyyne $\pi\pi^*$ states and the ICT state differ by two one-electron promotions. Despite the small mixing, the fact that the ICT band intensity remains high for all n suggests that charge transfer through the conjugated linker is very efficient even for $n = 3$. Qualitatively the diphenylpolyyne linking group is acting as a molecular wire.

As previously mentioned the emission quantum yields (Figure 3) decrease precipitously as n goes from one to three. This, taken with the observation that the extinction coefficients for the ICT band remain relatively constant, suggests that the rate constant for nonradiative decay increases with polyyne length. This enhanced nonradiative decay could be due to intersystem crossing or internal conversion of the singlet ICT state.[12]

In summary, we have prepared a series of new donor-acceptor molecules in which the energies and intensities of the ICT electronic transitions are relatively independent of the length of the polyyne linking chain while the nonradiative decay rate shows dramatic enhancement with increasing linker length.

Acknowledgment. We thank Dr. David Beratan for helpful discussions. The research reported in this paper was performed by the Jet Propulsion Laboratory, California Institute of Technology, as part of its Innovative Space Technology Center, which is sponsored by the Strategic Defense Initiative Organization/Innovative Science and Technology through an agreement with the National Aeronautics and Space Administration (NASA).

---

(9) (a) Lakowicz, J. R. *Principles of Fluorescence Spectroscopy*; Plenum Press: New York, 1983. (b) Mataga, N.; Kubota, T. *Molecular Interactions and Electronic Spectra*; Marcel Dekker: New York, 1970.

(10) Twisting of the two phenyl rings of these molecules may be an important factor in describing the excited state and its dynamics, as it is in the ICT states of some other molecules (Rettig, W. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 971-988. Bonacic-Koutecky, V.; Koutecky, J.; Michl, J. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 170-189).

(11) A detailed study of the solvent dependence is currently underway. We have not been able to detect any emission from solution in more polar solvents such as acetonitrile.

(12) As n increases the higher density of vibrational states in the ground electronic state could yield faster internal conversion. However, increases in n could also be expected to yield faster intersystem crossing. This could be due to the greater charge separation in the ICT allowing rapid spin decorrelation from singlet to triplet ICT state or due to a decreased energy gap between ICT and $^3\pi\pi^*$ as a result of the lowering of the energy of $^3\pi\pi^*$ with increasing n.

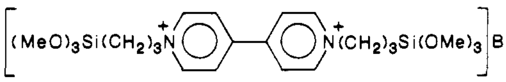
High Surface Area Catalysts for H_2 Reduction of an Enzyme: Reduction of NAD^+ to NADH

Shuchi Chao and Mark S. Wrighton*

Department of Chemistry
Massachusetts Institute of Technology
Cambridge, Massachusetts 02139

Received May 11, 1987

We report results which show that enzymes, formate dehydrogenase (FDH, MW $\approx$ 320 000)[1] and lipoamide dehydrogenase (LipDH, MW$\approx$100,000)[2] can equilibrate with the redox polymer derived from I[3] anchored to high surface area SiO_2,



I

$[SiO_2]–(PQ^{2+})_n$,[4] eq 1 and 2. Further, by impregnating the

$$[SiO_2]–(PQ^{2+})_n + {}^1/_2 n HCO_2^- \xrightleftharpoons{\text{FDH}} [SiO_2]–(PQ^+)_n + {}^1/_2 n CO_2 + {}^1/_2 n H^+ \quad (1)$$

$$[SiO_2]–(PQ^{2+})_n + {}^1/_2 n \text{NADH} \xrightleftharpoons{\text{LipDH}} [SiO_2]–(PQ^+)_n + {}^1/_2 n \text{NAD}^+ + {}^1/_2 n H^+ \quad (2)$$

---

(1) Thauer, R. K.; Fuchs, G.; Jungermann, K. in *Iron-Sulfur Proteins*; Lowenberg, W., Ed.; Academic Press: New York, 1977; Vol. 3, p 121. FDH was obtained commercially from Sigma Chemical Co. (FDH, ECl. 1.2.1.2., from *Pseudomonas oxalaticus*, $\sim$0.3 unit activity per mg protein).

(2) (a) Barman, T. E., *Enzyme Handbook*; Springer Verlag: New York, 1969; Vol. 1, p 203. (b) Massey, V. In *The Enzymes*, 2nd ed.; Boyer, P. D., Lardy, H., Myrback, K., Eds.; Academic Press: New York, 1963; Vol. 7, p 279. LipDH was obtained commercially from Sigma Chemical Co. (LipDH, EC1.4.6.3, Type III from porcine heart, $\sim$100 units activity per mg protein, or Type V from Torula yeast, $\sim$25 units activity per mg protein).

(3) Bookbinder, D. C.; Wrighton, M. S. *J. Electrochem. Soc.* **1983** *130*, 1080.

(4) (a) Chao, S.; Stalder, C. S.; Summers, D. P.; Wrighton, M. S. *J. Am. Chem. Soc.* **1984**, *106*, 2723. (b) Bookbinder, D. C.; Lewis, N. S.; Wrighton, M. S. *J. Am. Chem. Soc.* **1981**, *103*, 7656 for modification of Pyrex glass with $(PQ^{2+}\cdot Pt)_n$. (c) SiO_2 used is from Alfa, 330 m^2/g, pretreated by heating to 300 °C for 48 h prior to refluxing with I in CH_3CN to effect formation of $[SiO_2]–(PQ^{2+})_n$, $\sim$70% by weight $(PQ^{2+}\cdot 2Br^-)$. Partial exchange of Br^- by $PtCl_4^{2-}$ followed by H_2 reduction in aqueous solution gives $[SiO_2]–(PQ^{2+}\cdot xPt)_n$ with a Pt loading of $\sim$0.5% by weight. $[SiO_2]–(DA^{2+}\cdot xPt)_n$ was prepared similarly where $(DA^{2+})_n$ is derived from hydrolysis of the nonredox active diammonium reagent *N,N′*-bis[3-(trimethoxysilyl)propyl]-*N,N,N′-,N′*-tetramethyl-1,6-hexanediammonium. Details of catalyst preparation are reported in a full paper: Chao, S.; Simon, R. A.; Mallouk, T. E.; Wrighton, M. S., submitted for publication.

0002-7863/87/1509-5886$01.50/0