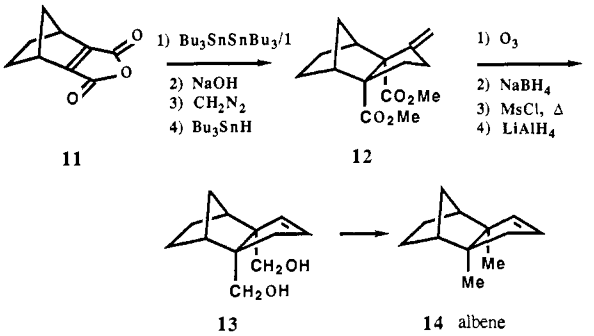
1, followed by standard initiation with AIBN, produced the corresponding (methylene)cyclopentane **3** (I = H) in 52% overall yield from methyl acrylate. As expected, attempts to convert **1** and **2** directly to **3** (I = H) by tin hydride treatment were not successful.

An illustration of the new method is provided by a total synthesis of the simple natural product albene (eq 2).[15] Atom transfer addition of **1** to **11** was followed by conversion of the anhydride to the dimethyl ester and reductive deiodination. By this sequence, diester **12** was isolated in 55% overall yield from **11**. Routine transformations provided **13** (32% overall), which has previously been deoxygenated[15b] to provide albene **14**. The yields of these intermediate steps have not been extensively optimized.



(2)

In summary, this atom transfer cycloaddition reaction provides an unusually direct method for the formation of substituted (methylene)cyclopentanes. Although modest yields (typically 40–60%) are the rule, the straightforward simplicity of this one-step route may make it attractive for synthetic applications. The unique advantages of control of the free-radical sequence by iodine atom transfer are apparent, and the design of other atom transfer based sequences will be reported in the near future.

**Acknowledgment.** We thank the National Institutes of Health (GM-33372) for funding of this work.

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## Electronic Transitions of Polyacenequinone Radical Anions in the 1-2 μm Region

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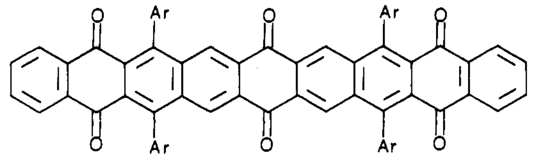
Studies from this laboratory have led to the syntheses of linear, polyquinoidal polyacenes like compound **1**.[1,2] It was proposed that, "...quinoidal derivatives would have interesting possibilities for substantially varying the electronic structure of a large molecular framework, and by appropriately choosing quinone-, semiquinone-, and hydroquinone-type moieties the reactivity and the optical, magnetic, and electrical properties could be controlled."[1] In this communication, we report initial results on the optical properties of such compounds, with emphasis on radical anions (semiquinones) of compounds like **1**, which have intense absorptions in the near infrared (NIR) region between 1 and 2 μm. To our knowledge good precedent for this observation is lacking. We suggest that these bands result from $\pi^*-\pi^*$ excitations, that the bands are characteristic of di- or polyquinones, not monoquinones, that they should be shifted to the IR region in suitable cases, and that such bands may be found in other anion-radicals of appropriate structure. It is further noted that these observations could lead to applications in optics or electrooptics.

**Table I.** Physical Properties of Semiquinones

| semiquinone | $-E^{\circ a}$ (mV, SCE) | $\lambda_{max}$ (nm) (log $\epsilon$)$^b$ |
|---|---|---|
| $1^{\bullet-}$ | 665, 981, 1265 | 1730 (4.43), 485 (4.11)<br>435 (4.17) |
| $2^{\bullet-}$ | 420, 920 | 1335 (4.50), 1130 (4.08)<br>430 (3.78), 400 (3.78) |
| $3^{\bullet-}$ | 256, 737 | 1560 (4.21), 1286 (3.80)<br>440 (3.68), 410 (3.62) |
| $4^{\bullet-}$ | -142, 586 | 900 (4.66), 805 (3.63)<br>485 (3.60), 450 (3.58) |
| $5^{\bullet-}$ | 608, 1412 | 480 (3.89), 410 (3.97)<br>390 (3.71) |
| $6^{\bullet-}$ | 960, 1565 | 595 (4.03), 390 (3.85) |
| $7^{\bullet-}$ | 1048, 1655 | 650 (3.95), 440 (3.45) |

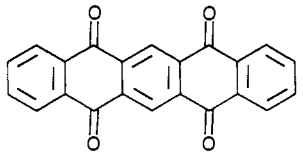
$^a$DMF, $Bu_4NBF_4$ at glassy carbon. Center of anodic and cathodic peak potentials, the first number is for $Q/Q^{\bullet-}$. $^b$In DMF, $Bu_4NBF_4$.

Compound **1** was reduced electrochemically in DMF solution, 0.1 M in tetrabutylammonium tetrafluoroborate, by using a carbon felt electrode in a simple 2-compartment cell. Cyclic voltammograms were obtained by using a small glassy carbon analytical electrode prior to bulk electrolysis. The voltammogram for **1** displays three separate one-electron reversible couples (see Table I) followed by a fourth quasi-reversible couple. The potential for bulk electrolysis was set several millivolts cathodic of the first couple. After passage of 1.2 Faradays/mol, the electrolysis current had dropped to near the background level, and the absorbance spectrum of the resultant solution was measured with the exclusion of oxygen. Under such conditions, the optical spectrum did not change with time. Either exposure to oxygen or electrochemical reoxidation of the solution regenerated **1**, which could be reisolated by extraction and flash chromatography.

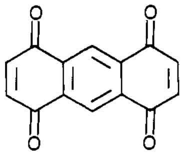


**1**

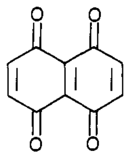
Ar = $(CH_3)_3C—C_6H_4$



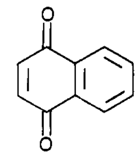
**2**



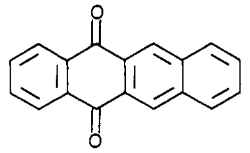
**3**



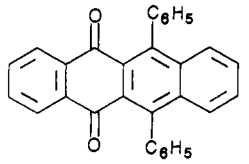
**4**



**5**



**6**



**7**

The absorption spectrum of **1** is quite ordinary. It shows the longest wavelength band at 440 nm, which is similar to the spectrum of the monoquinone model **7**.[3] The absorption spectrum

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(1) Thomas, A. D.; Miller, L. L. *J. Org. Chem.* **1986**, *51*, 4160.
(2) Christopfel, W. C.; Miller, L. L. *J. Org. Chem.* **1986**, *51*, 4169.

(3) UV–vis spectra in $CH_2Cl_2$ **7**: 245 (43 000), 296 (26 500), 394 (5500); **1**: 275 (46 000), 318 (116 000), 440 (26 000).

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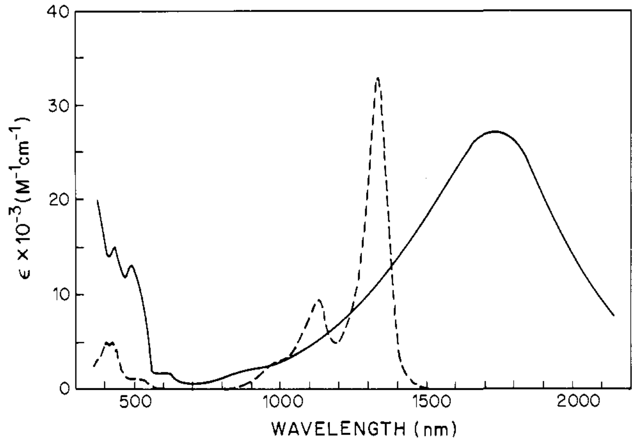

**Figure 1.** Absorption spectra for $1^{\bullet-}$ (—) and $2^{\bullet-}$ (– –) in DMF, $Bu_4NBF_4$.

of $1^{\bullet-}$ (Figure 1) is quite *unordinary*. It shows a band with $\lambda_{max}$ at 1730 nm (0.74 eV) $\epsilon = 27\,000$.

Few semiquinone spectra are reported in the literature,[4] so in order to understand this observation, a number of model compounds have been prepared and studied by using the above method. Electrochemically, each diquinone showed two reversible, one-electron couples and a third quasi-reversible couple. The monoquinones gave two reversible couples. Preparative scale reduction gave stable semiquinones. The optical spectra are described in Table I. It was found that monoquinone anion-radicals do not exhibit these intense long wavelength bands. Simple di- and triquinone anion-radicals do show such bands. There seems to be a trend to lower transition energies for the diquinone anion radicals as the quinones are spaced farther apart, and it may be that this observation could be capitalized on to push the absorption maximum farther into the IR.

Because the neutral quinones do not have these 1–2 μm bands, it is proposed that the absorption originates from excitation of the odd electron of the anion-radical. In this wavelength region, intramolecular intervalence-transfer transitions of mixed-valence species are commonly observed.[5] Since the radical-anions of diquinones (or triquinones) might be envisaged to have a quinone and a semiquinone site, they could, in principle, qualify as mixed-valence species.[6] As such the spectra of $1^{\bullet-}$ and $2^{\bullet-}$ suggest that the two sites are fully delocalized (type III mixed-valence). Thus, the sharpness of the bands and the high absorption intensity at long wavelength indicate that the two mixed-valence sites are very similar in structure and strongly interacting. A second possible interpretation for the band is from intermolecular charge transfer. Evidence against this origin is provided by linear Beer's law behavior for $2^{\bullet-}$ in DMF over the concentration range $10^{-5}$–$5 \times 10^{-4}$ M. Evidence against either intermolecular or intramolecular charge transfer comes from the lack of solvent dependence.[7] With use of $2^{\bullet-}$ it was shown that the band maximum at 1335 nm was unaffected (±10 nm) as the medium was changed from DMF, $Bu_4NBF_4$ to DMF, $LiClO_4$; THF, $Bu_4NBF_4$ and $CHCl_3$, $Bu_4NBF_4$. With use of $1^{\bullet-}$ the band maximum was the same in DMF or $CH_2Cl_2$ containing $Bu_4NBF_4$.

It is suggested that these transitions involve $\pi^*$–$\pi^*$ excitation of the odd electron, which is initially held in a delocalized orbital. In agreement with this assignment for $2^{\bullet-}$, $3^{\bullet-}$, and $4^{\bullet-}$ are ESR spectra showing the expected symmetry. In addition the IR spectrum of $2^{\bullet-}$ $Bu_4N^+$ as a KBr disk shows no quinone carbonyl. Finally, ab initio calculations on $3^{\bullet-}$, $4^{\bullet-}$, and $5^{\bullet-}$ confirm that $\pi^*$–$\pi^*$ transitions are involved.[8] These restricted Hartree–Fock calculations were performed for the ground and excited states of the anion-radicals and gave a satisfactory account of the trends in transition energies.

There is some concern over extrapolating the conclusions from $2^{\bullet-}$, $3^{\bullet-}$, and $4^{\bullet-}$ to $1^{\bullet-}$ especially in view of the width of the band for $1^{\bullet-}$ compared to $2^{\bullet-}$. In this regard we note that the spectrum of $1^{2-}$ is unusual and entirely different from that of $2^{2-}$. Most piquant is the $1^{2-}$ spectrum which shows $\lambda_{max}$ 1.9 μm ($\epsilon$ 75 000). Further explication of the origin of these spectra, a definition to the scope of this phenomenon, and applications to switchable optical devices will be reported.

**Acknowledgment.** This work was supported by the NSF and ONR. Thomas H. Jozefiak held a fellowship from the Proctor and Gamble Co. Compound **1** was supplied by Dr. W. Christopfel. Data on $7^{\bullet-}$ were from Stan Rak.

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[8] Performed by Professor Jan Almlof and Martin Feyereisen. Details will be provided in the full paper.

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## Greatly Enhanced Second-Order Nonlinear Optical Susceptibilities in Donor–Acceptor Organic Molecules

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It has been generally recognized[1,2] that donor–acceptor substituted organic compounds such as benzenes, stilbenes, and azo dyes possess large molecular second-order nonlinear optical susceptibilities (β). Measurements and calculations of second-order susceptibilities of these organic materials have largely been limited to compounds containing substituents whose donating or accepting abilities do not exceed those of amino or nitro, respectively.[1,2] Herein, we report that β can be increased substantially through the use of dicyanovinyl or tricyanovinyl as acceptor and/or dithiolylidinemethyl as donor groups. The use of cyanovinyl acceptors in compounds for nonlinear optics has been previously suggested.[3]

Table I lists a representative sample of the molecules we have investigated. Compounds **1** and **6** were obtained commercially, while **2**[4] and **3**[5] were synthesized as previously described. The synthesis of **7** had been noted[6] without details. Compounds **4** and

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[†] AT&T Bell Laboratories.

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