Conf-920444--27

PNL-SA--20358

DE92 012353

ELECTRONIC STRUCTURE AND PHOTOPHYSICAL PROPERTIES OF POLYIMIDES

J. P. LaFemina
S. A. Kafafi

April 1992

Presented at the
American Chemical Society 1992 Spring Meeting
April 5-10, 1992
San Francisco, California

Work supported by
the U.S. Department of Energy
under Contract DE-AC06-76RLO 1830

Pacific Northwest Laboratory
Richland, Washington 99352

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

MASTER

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

To be presented at the Spring 1992 ACS Meeting in session
Polymer Photophysics: Fundamentals and Applications

Electronic Structure and Photophysical Properties of Polyimides

John P. LaFemina*, *Molecular Science Research Center, Pacific Northwest Laboratory, P.O. Box 999, Richland, WA 99352*

Sherif A. Kafafi, *The Johns Hopkins University, Division of Environmental Chemistry, 615 North Wolfe Street, Baltimore, MD 21205*

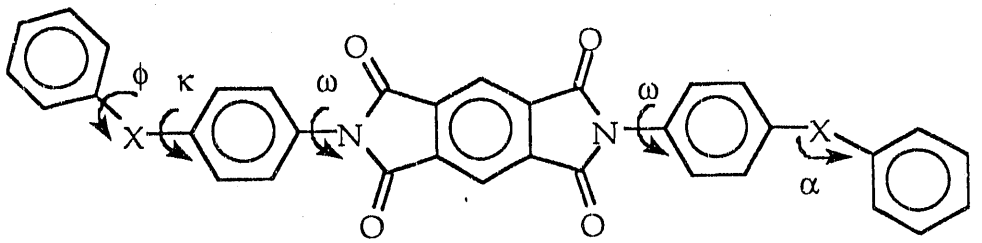
I. Introduction

Aromatic polyimides have found wide-ranging application in the electronics industry because of their superior thermal and mechanical properties, and low dielectric constant[1]. These polymers are also photoconductive, both undoped and doped, although their utility in photoconductor technologies has been limited by the low quantum yield of photogenerated conduction electrons. Experimental[2,3,4] and theoretical[5,6,7] examinations of PMDA-ODA (pyromellitic dianhydride-oxydianiline) polyimide (Figure 1) have led to the conclusion that intramolecular charge transfer (ICT) from the ODA to the PMDA moiety plays an important role in determining the photophysical properties of the polymer films, including the intrinsic photoconduction and laser etching processes, as well as the ultraviolet absorption and emission spectra. Moreover, because the ICT is sensitive to the conformation of the polymer backbone, it can be utilized as a probe of the polymer conformation[8]. Our purpose in this paper is to examine the relationship between the structure and photophysical properties of a series of isoelectronic aromatic polyimides, shown in Figure 1.

II. Method

The conformations of the polyimide oligomers shown in Figure 1 were determined via geometry optimization using the AM1 semiempirical quantum chemical method[9,10]. The density of valence state (DOVS) and ultraviolet absorption spectra (UVA) were computed using the spectroscopically

parametrized CNDO/S3 model[11]. Parameters were taken from previous studies[5-7].



X = - O (PMDA-ODA)

- NH (PMDA-ADA)

- CH_2 (PMDA-MDA)

Figure 1. Oligomer used to model the aromatic polyimides PMDA-ODA, PMDA-ADA, and PMDA-MDA.

III. Results and Discussion

A. Polymer Conformation

With respect to ICT, the four angles defined in Figure 1 are the most important geometric parameters. Table I lists the values of these angles as determined by AM1 energy minimization computations. It is interesting to note the angle between the PMDA moiety and its adjacent phenyl rings is unaffected by the substitutions in the diamine moiety. Consequently, any changes in ICT in these materials will arise from the changing conformation about the substitution site. It is clear from the data in Table I, as well as the fact that the methyl carbon is completely saturated, that PMDA-MDA will have no pi-electron delocalization across the methyl linkage. PMDA-ODA, with a torsional orientation of ϕ=64° will have a slight amount, while PMDA-ADA (ϕ=50°) will have more.

Table I. Values of the torsional angles defined in Figure 1 as determined via AM1 geometry optimizations for PMDA-MDA, PMDA-ODA, and PMDA-ADA.

Polymer	ϕ	κ	ω	α
PMDA-MDA	90°	±60°	30°	114°
PMDA-ODA	64°	0°	30°	117°
PMDA-ADA	50°	37°	30°	123°

B. Electronic Structure

The density of valence states computed using the CNDO/S3 model is shown in Figure 2. The most striking feature is the shift to lower binding energies of the highest energy peak as one moves from PMDA-MDA to PMDA-ODA to PMDA-ADA. This peak represents the nearly degenerate highest-occupied molecular orbital (HOMO) and the subjacent HOMO, and the shift correlates with the diminishing torsional angle, ϕ, about the subsitution site and the increase in electron delocalization about the diamine linkage. An examination of the orbital electron densities of the HOMO and subjacent HOMO confirm that the destabilization of these orbitals is due to an increased delocalization across the diamine linkage, which for these orbitals is an antibonding, or destabilizing, interaction. The effect of this shift in orbital energies on the optical absorption spectra is discussed in the next section.

C. Optical Absorption Spectra

The low-energy peak in the UVA spectra of PMDA-ODA corresponds to an ICT π-π^* transition from the HOMO to the superjacent lowest-unoccupied molecular orbital (LUMO)[5]. Because the superjacent LUMO has almost no orbital electron density at the substitution site, its energy is nearly unaffected in all three systems. Consequently, the destabilization of the HOMO should cause a corresponding blue shift of the ICT peak. The computed optical absorption spectra for the three systems is shown in Figure 3 where the predicted blue shift is clearly seen.

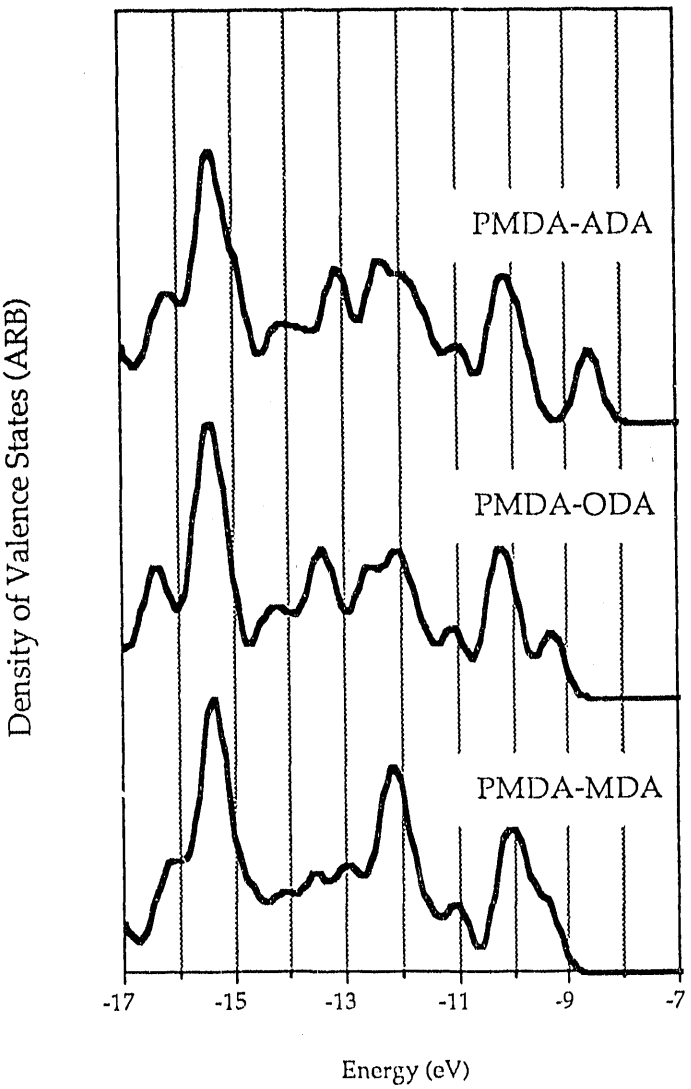


Figure 2. Computed DOVS for PMDA-MDA, PMDA-ODA, and PMDA-ADA

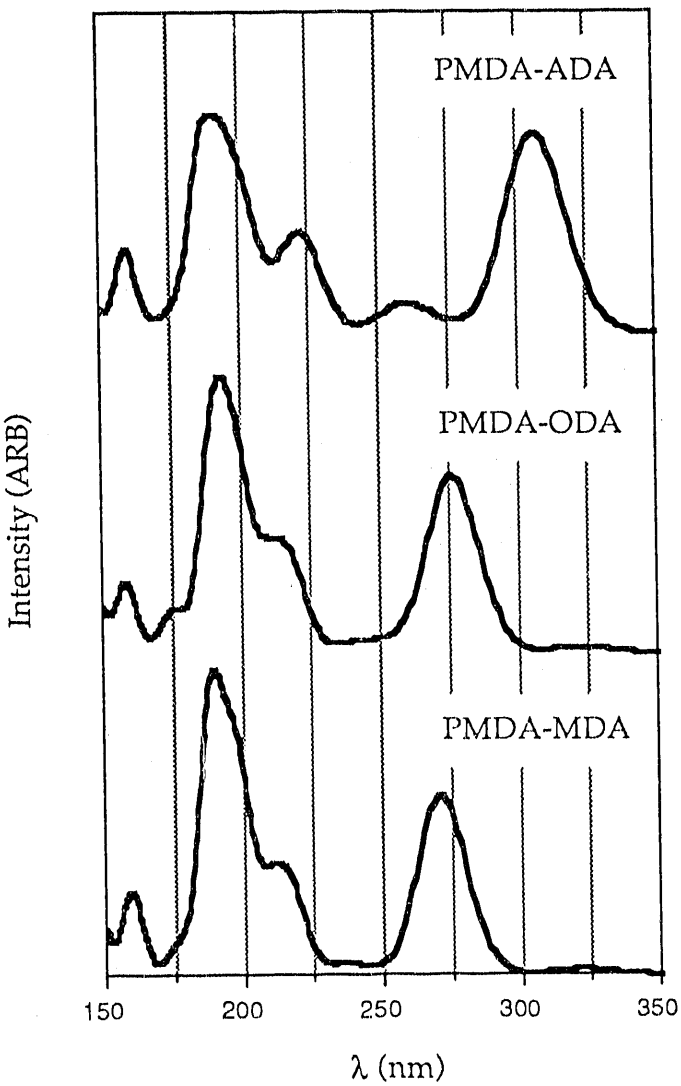


Figure 3. Computed optical absorption spectra for PMDA-MDA, PMDA-ODA, and PMDA-ADA

IV. Synopsis

The quantum mechanical AM1 and CNDO/S3 models were used to examine the effect of isoelectronic substitutions on the conformation, electronic structure, and optical absorption spectra for a series of aromatic polyimides. An analysis of the geometric changes at the substitution site and its effect on the electronic structure allowed for the prediction of changes in the ICT band of the optical absorption spectra.

Acknowledgements

Dr. S.A. Kafafi acknowledges the financial support of the A. Mellon Foundation. We are grateful to Dr. C.B. Duke for generously allowing the use of his CNDO/S3 computer codes. The Pacific Northwest Laboratory is operated for the US Department of Energy by Battelle Memorial Institute under contract DE-AC06-76RLO 1830.

References

1. See for example: (a) "Recent Advances in Polyimide Science and Technology", W.D. Weber and M.R. Gupta, Eds. (Society of Plastics Engineers, Mid-Hudson Section, 1987), and (b) "Polyimides", K.L. Mittal, Ed. (Plenum Press, New York, 1984).

2. S.C. Freilich, Macromolecules 20,973 (1987).

3. S.C. Freilich and K.H. Gardner, in "Proceedings of the Third International Conference on Polyimides", Ellenville, NY (November 1988).

4. E.D. Wachsman and C.N. Frank, Polymer 29,1191 (1988).

5. J.P. LaFemina, G. Arjavalingam, and G. Hougham, J. Chem. Phys. 90,5154 (1989).

6. J.P. LaFemina, Chem. Phys. Lett. 159,307 (1989).

7. G. Arjavalingam, G. Hougham, and J.P. LaFemina, Polymer 31,840 (1990).

8. J.M Salley, T. Miwa, and C.W. Frank, in "High Temperature Polymers for Microelectronics", D.Y. Yoon, D.T. Grubb, and I. Mita, Eds. (Materials Research Society, Pittsburgh, 1991).

9. (a) M.J.S. Dewar, E.G. Zoebisch, E.F. Healy, and J.J.P. Stewart, J. Am. Chem. Soc. 107,3902 (1985), (b) M.J.S. Dewar and K.M. Dieter, J. Am. Chem. Soc. 108,8075 (1986).

10. S.A. Kafafi, J.P. LaFemina, and J.L. Nauss, J. Am. Chem. Soc. 112,8742 (1990).

11. (a) N.O. Lipari and C.B. Duke, J. Chem. Phys. 63,1748 (1975), (b) C.B. Duke, N.O. Lipari, W.R. Salaneck,and L.B. Schein, *ibid* 63,1758 (1975), (c) N.O. Lipari and C.B. Duke, *ibid* 63,1768 (1975).

END

DATE
FILMED
6/12/92