JOURNAL OF PHYSICAL ORGANIC CHEMISTRY, VOL. 6, 531–534 (1993)

CALCULATION OF NON-LINEAR OPTICAL PROPERTIES OF PYRIDINIUM CYCLOPENTADIENYLIDES

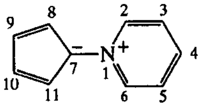
JULIANTO PRANATA* AND CHRISTOPHER J. MURRAY
Department of Chemistry and Biochemistry, University of Arkansas, Fayetteville, Arkansas 72701, U.S.A.

Finite field/PM3 calculations of the dipole moments, polarizabilities, hyperpolarizabilities, and second-order hyperpolarizabilities of pyridinium cyclopentadienylide and some nitro and amino derivatives suggest that these compounds are good candidates for non-linear optical materials.

INTRODUCTION

There has been a considerable effort directed towards the development of materials possessing non-linear optical properties, and organic compounds have been recognized as excellent candidates for such materials.[1] The enormous variety of organic molecules, together with the achievements of organic synthesis, suggest that it may be possible to design materials to fit the desired properties. In this process computational studies can play an important role in that they can predict the properties of new molecules.

We recently reported the use of derivatives of pyridinium cyclopentadienylide (PC) as a probe for measuring the dielectric constant of enzyme active sites.[2] This compound exhibits many of the characteristics of a molecule with significant non-linear optical properties. It has a conjugated π-system, has charge-transfer character and its electronic spectrum exhibits solvatochromism,[3] indicating a significant difference in the dipole moments of the ground and excited states.



We have investigated the non-linear optical properties of PC using the finite field method[4] as implemented in PM3 semi-empirical molecular orbital calculations.[5] Calculations of this type have been performed by Matsuzawa and Dixon for an extensive list of compounds, and comparisons have been made with experimental measurements.[6,7] The results show a good correlation between calculated and observed quantities. Thus, the finite field/PM3 method is a fast, inexpensive and fairly reliable method for calculating non-linear optical properties of organic molecules.

In addition to the parent compound, we have also looked at a few mono- and disubstituted derivatives. The substituents are nitro and amino groups, to represent typical π-electron acceptors and donors, which may serve to enhance or diminish the nonlinear optical properties.

Our objective in this study was not to predict accurately the non-linear optical properties of PC and its derivatives. Too many experimental parameters that are important in non-linear optics, such as crystal packing (if crystals are used), solvent properties (if solutions are used) and the wavelength of light used, were not considered in the calculations. Rather, our intention was to explore the possibility that these unusual molecules have significant and perhaps useful non-linear optical properties. For this purpose, we believe that the finite-field/PM3 method is suitable.

COMPUTATIONAL METHODS

The calculations were performed using the MOPAC program.[8] The finite field method involves the calculation of the molecular electronic energy in the presence of an external electric field **F**, which can be expressed as[4]

$$E(\mathbf{F}) = E(0) - \sum_i \mu_i F_i - (1/2) \sum_{i,j} \alpha_{ij} F_i F_j - (1/6) \sum_{i,jk} \beta_{ijk} F_i F_j F_k - (1/24) \sum_{i,j,k,l} \gamma_{ijkl} F_i F_j F_k F_l - \cdots \quad (1)$$

---

[*] Author for correspondence.

0894-3230/93/090531-04$07.00

Received 10 March 1993
Revised 26 May 1993

where $E(0)$ is the energy with no field present, F_i are the components of the external field, μ_i are the components of the dipole moment vector, α_{ij} are the components of the polarizability tensor, β_{ijk} are the components of the hyperpolarizability tensor and γ_{ijkl} are the components of the second-order hyperpolarizability tensor. By computing the energy in several different fields, all the tensor components can be calculated.

An alternative method uses the dipole moment expansion[4]

$$\mu_i(\mathbf{F}) = \mu_i(0) + \sum_j \alpha_{ij}F_j + (1/2) \sum_{j,k} \beta_{ijk}F_jF_k + (1/6) \sum_{j,k,l} \gamma_{ijkl}F_jF_kF_l + \cdots \quad (2)$$

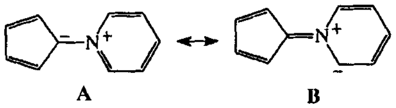
where $\mu_i(0)$ is a component of the permanent dipole moment and other quantities are as defined before. Both methods are employed in the MOPAC program. The values reported here are those obtained from the energy expansion; the dipole expansion gave similar values.

All structures were fully optimized, and the optimized structures were subjected to vibrational frequency calculations to ensure that they correspond to local minima. The finite field computations were performed at the optimized geometries. Except for the frequency calculations, the PRECISE option in the MOPAC program was selected for all calculations. The calculations were performed on an HP/Apollo Series 700 workstation and a Silicon Graphics Indigo R4000 workstation.

RESULTS AND DISCUSSION

A common feature of molecules possessing non-linear optical properties is the presence of a conjugated π-electron system. Computational studies have demonstrated the trend of increasing polarizabilities and hyperpolarizabilities with increasing conjugation length.[7] For PC, maximum conjugation would be achieved in a planar structure.

It is reasonable to expect PC itself to be planar. A resonance structure can be drawn where the exocyclic C—N bond is a double bond. Although not explicitly shown, the resonance structure **A** is intended to imply delocalization of the negative charge in the cyclopentadienyl ring and the positive charge in the pyridinium ring. In the resonance structure **B**, the negative charge is now delocalized in a pentadienyl fragment of the six-membered ring, while the positive charge is localized on the nitrogen. PM3 calculations support this idea of resonance. The optimized structure is indeed planar, and the C—N bond length is 1·36 Å, indicating partial double bond character; for example, the C—N bond in amides (generally accepted to have partial double bond character) is about 1·40 Å, whereas for *N*-alkylpyridiniums we found the C—N bond length to be 1·48–1·50 Å. In addition, the barrier for rotation around this bond was estimated to be about 15 kcal mol^{-1} (1 kcal = 4·184 kJ); this was done by calculating the energy at a geometry where the two rings were constrained to be perpendicular. (In fact, we computed complete torsional profiles for the molecules discussed here, by performing a series of constrained geometry optimizations with the C—N torsion constrained at 30° intervals. For all of them, the maximum energy occurred at 90°.)



The presence of an electron-donating or -withdrawing substituent can alter the situation. An electron-withdrawing nitro group on the five-membered ring would favor the resonance structure **A** owing to further delocalization of the negative charge present in the five-membered ring, and result in reduced double bond character in the C—N bond. The opposite effect would occur if the nitro group were in the 2-, 4- or 6-(*ortho* or *para*) position of the six-membered ring; in this case, the resonance structure **B** would be favored. The 3- and 5- (*meta*) positions, however, are out of conjugation, and substitutions at these positions are not expected to have a large effect.

An electron-donating amino substituent at the *ortho* and *para* positions of the six-membered ring would favor the resonance structure **A**; the positive charge can be delocalized into the amino group. Once again, substituents at the *meta* positions are out of conjugation and would not have a large effect. In the resonance structure **B** the positive charge is localized on nitrogen and cannot be delocalized further, whether or not there are electron-donating substituents. In addition, there is no reasonable resonance structure that places the positive charge in the five-membered ring, so amino substituents on it would not have a large effect.

Another issue is steric repulsion. Even in the parent compound, the hydrogens at positions 2 and 8 and at positions 6 and 11 are spatially close, although not enough to cause steric congestion. Replacing any of them with larger substituents could have serious steric consequences. This effect may be large enough to disfavor the coplanar orientation between the rings.

We investigated these issues using PM3 calculations on PC and monosubstituted derivatives. The results, shown in Table 1, are generally consistent with the foregoing analysis. The amino group is pyramidal, the same situation as observed in arylamines. In most cases, the nitro group is coplanar with the ring to which it is attached. The exception is when the nitro group is at the

2-position, where steric factors force a non-planar orientation of the nitro group in addition to twisting around the C—N bond.

Actually, the issue that most concerns us is not whether the rings are coplanar, but rather the size of the rotational barriers. When small barriers are involved, any calculated property (including non-linear optics) would need to be conformationally averaged. Rather than worry about this additional complication, we decided to focus on those derivatives which are expected to prefer strongly a planar structure. The derivatives are those listed in Table 2. PM3 calculations predict all of them to be planar and to have rotation barriers of 15 kcal mol^{-1} or greater. Some other disubstituted derivatives, and also some of the monosubstituted derivatives shown in Table 1, are also predicted by PM3 calculations to prefer strongly a planar or near-planar geometry. Others have such small rotation barriers that they can be expected to undergo free rotation. Still others are in between. We elected to be conservative and limit this report to the derivatives in Table 2. This is not to say that other derivatives are unsuitable for non-linear optics; it just means that we are less confident that the computational methodology employed here would give reliable results for these other compounds.

Table 1. Conformational results for PC and monosubstituted derivatives

Substituent	Twist angle (°)[a]	C—N bond length (Å)[a]	Barrier (kcal mol^{-1})[b]
None	0	1·36	14·6
2-Amino	15	1·38	5·4
3-Amino	0	1·36	14·3
4-Amino	0	1·37	12·0
8-Amino	0	1·37	10·9
9-Amino	0	1·36	15·1
2-Nitro	12	1·35	13·5
3-Nitro	0	1·36	17·9
4-Nitro	0	1·35	21·1
8-Nitro	12	1·41	3·4
9-Nitro	0	1·38	8·3

[a] At the PM3 optimized geometry.

[b] Estimated by calculating the energy at a geometry where the two rings were constrained to be perpendicular.

The calculated dipole moments, polarizabilities, hyperpolarizabilities and second-order hyperpolarizabilities are given in Table 2. In most cases, the dipole moment direction is approximately along the long axis of the molecule, with the five-membered ring at the negative end. This is consistent with the resonance structure **A**. The exceptions are when there are nitro substituents. In these cases, the nitro group is approximately at the negative end of the dipole. Consequently, the 4-nitro-substituted compounds have a dipole moment vector aligned in the opposite direction to that of the parent compound, whereas the 3-nitro-substituted compounds have a dipole moment almost perpendicular to the molecule's long axis.

The value given for α is the isotropic component of the polarizability, obtained from the calculated α tensor:

$$\alpha = \sum_i \alpha_{ii}/3 \tag{3}$$

As shown in Table 2, all of the molecules are highly polarizable, more than many other non-linear optical materials.[6] The presence of substituents does not have a large effect on the polarizability; this was also observed in other materials.[6]

The listed value for β is the vector component of the hyperpolarizability along the dipole moment, as obtained from the calculated β tensor:

$$\beta = 3/5 \sum_i \beta_i \mu_i / \| \mu \| \tag{4}$$

$$\beta_i = \sum_j \beta_{ijj} \tag{5}$$

The negative sign for some of the entries can be interpreted as indicative of the change in dipole moments between the ground and excited states. In going from the ground state to the excited state, the electron flow

Table 2. Results of finite field/PM3 calculations on PCs

Substituent	μ (D)	α (10^{-23} esu)	β (10^{-30} esu)	μ (10^{-36} esu)
None	4·19	3·62	−12·22	−9·04
3-Amino	5·13	3·97	−9·47	−7·35
9-Amino	3·76	4·19	−24·45	2·35
3-Nitro	4·25	4·17	−2·53	−8·33
4-Nitro	4·01	4·39	11·06	−0·65
3-Amino-4-nitro	3·06	4·73	10·84	1·11
3-Amino-5-nitro	5·57	4·54	−0·70	−6·24
9-Amino-3-nitro	4·43	4·83	4·81	8·39
9-Amino-4-nitro	5·49	5·14	30·12	25·38
10-Amino-3-nitro	4·41	4·83	−2·76	8·06

is apparently always from the five- to the six-membered ring. For most of the compounds, this is in a direction opposite to the ground-state dipole moment, hence the negative sign of β. Consistent with this interpretation, the dipole moment of PC in the excited state has been calculated to be considerably smaller than in the ground state.[9] For the 4-nitro-substituted compounds, however, the ground-state dipole moment is in the opposite direction. The electron flow is still from the five- to the six-membered ring, but now this serves to enhance the dipole moment, resulting in positive β values. For 3(or 5)-nitro-substituted compounds, the direction of electron flow is almost perpendicular to the ground-state dipole moment, resulting in much smaller magnitudes of β. (Recall that β is the component of the hyperpolarizability tensor along the dipole moment direction; equations (4) and (5).)

The listed value for γ is the mean value obtained from the calculated γ tensor:

$$\gamma = 4/6 \sum_{i,j} \gamma_{iijj}/5 \tag{6}$$

The factor of 4/6 is necessary to allow direct comparison with experimental measurements.[6]

The calculated values of β and γ for 4-nitroaniline (a compound whose non-linear optical properties have been extensively studied, both theoretically and experimentally) are $6{\cdot}3 \times 10^{-30}$ and $12{\cdot}5 \times 10^{-36}$ esu, respectively (experimental values: $9{\cdot}2 \times 10^{-30}$ and 15×10^{-36}).[6] The calculated β values for many of the PCs are remarkably large in comparison. The calculated γ values are not as remarkable, but still promising. A survey of organic materials whose non-linear optical properties have been studied in the past reveals that most are essentially benzene derivatives. The time has come to extend the search for non-linear optical materials to include more 'exotic' compounds, such as the PC derivatives discussed here, or the azulenes and sesquifulvalenes suggested by Morley.[10]

REFERENCES

1. D. J. Williams (Ed), *Nonlinear Optical Properties of Organic and Polymeric Materials.* ACS Symposium Series, Vol. 233, American Chemical Society, Washington, DC (1983); D. S. Chemla and J. Zyss (Eds), *Nonlinear Optical Properties of Organic Molecules and Crystals.* Academic Press, New York (1987); P. N. Prasad and D. J. Williams, *Introduction to Nonlinear Optical Effects in Molecules and Polymers.* Wiley, New York (1991).
2. R. Kanski and C. J. Murray, *Tetrahedron Lett.* **34**, 2263 (1993).
3. E. M. Kosower and B. G. Ramsey, *J. Am. Chem. Soc.* **81**, 856 (1959).
4. H. A. Kurtz, J. J. P. Stewart and K. M. Dieter, *J. Comput. Chem.* **11**, 82 (1990).
5. J. J. P. Stewart, *J. Comput. Chem.* **10**, 209, 221 (1989).
6. N. Matsuzawa and D. A. Dixon, *J. Phys. Chem.* **96**, 6232 (1992).
7. For some other calculations using the finite field method and semi-empirical MO calculations, see G. R. J. Williams, *J. Mol. Struct. (Theochem)* **151**, 215 (1987); H. A. Kurtz, *Int. J. Quantum Chem., Quantum Chem. Symp.* **24**, 791 (1990); N. Matsuzawa and D. A. Dixon, *J. Phys. Chem.* **96**, 6241 (1992); N. Matsuzawa and D. A. Dixon, *Int. J. Quantum Chem.* **44**, 497 (1992); Y. J. Lu and S. L. Lee, *Int. J. Quantum Chem.* **44**, 773 (1992).
8. J. J. P. Stewart, *MOPAC 6.00, QCPE Program No. 455* (1990).
9. M. M. Karelson and M. C. Zerner, *J. Phys. Chem.* **96**, 6949 (1992).
10. J. O. Morley, *J. Am. Chem. Soc.* **110**, 7660 (1988).