

resented by unrestricted Hartree-Fock wave functions, and our calculated dissociation energies should be reasonable estimates (± 10 kcal/mol) for these species.

Natural population and natural bond orbital analyses^{47,48} of the various magnesium oxide species are summarized in Figure 4.

In both singlet and triplet states of MgO, the oxygen charges are close to -1.0. Hence, representations like Mg=O are inappropriate. Singlet-triplet splitting is small (0.326 eV),³² and the covalent coupling of the second pair of electrons is very weak. This weak coupling of the second pair of electrons allows MgO to bind an additional Mg atom to give the linear Mg-O-Mg molecule. The oxygen and magnesium charges in Mg-O-Mg are quite close to -2.0 and +1.0, respectively (at HF/6-311+G*). Hence, the charge distribution is similar to that in Na₂O. The two extra electrons in Mg₂O (vs Na₂O) are located on the Mg atoms. Coupling of these two electrons is also very weak (the singlet-triplet splitting is 0.15 eV at QCISD(T)/6-311+G(3df)). Both MgO and Mg₂O may be represented approximately as Mg¹⁺O¹⁻ and Mg¹⁺O²⁻Mg¹⁺. Therefore, a linear geometry is expected for Mg₂O on the basis of electrostatics. The dissociation energies increase in going from MgO (51.7 kcal/mol) to Mg₂O (74.5 kcal/mol (QCISD(T)/6-311+G(3df)+ZPE)). The structure and stability of the hyperstoichiometric Mg₂O molecule are largely due to the ionic nature of the bonding.

Bonding Mg-Mg interactions do contribute to the stability of Mg₃O. However, due to the low energy of the Mg-Mg bond, the dissociation energy of Mg₃O (into Mg₂O + Mg) is only 26.7 kcal/mol at QCISD(T)/6-311+G*+ZPE. This value is quite close to the dissociation energy of Al₃O (into Al₂O + Al) (19.9

kcal/mol at PMP4SDTQ/6-311+G*), where metal-metal interactions contribute to the stability.²⁰ While the ligand-ligand overlap population is even larger in the case of Mg₄O (*D*_{2d}, ¹A₁), the Mg-Mg distances are forced to be too short. This leads to increased ligand-ligand electrostatic repulsion. Hence, the dissociation energy of Mg₄O (*D*_{2d}, ¹A₁) into Mg₃O + Mg is quite low. In contrast, Al₄O (*D*_{4h}, A_{1g}) is very stable.²⁰ The Al-Al bond distance in square planar Al₄O is close to the optimum value (e.g., as in H₂AlAlH₂).⁴⁵

Conclusions

The main conclusions of this study are the following: (1) The hypermagnesium Mg₂O, Mg₃O, and Mg₄O molecules are stable toward all possible dissociation modes. However, in contrast to Mg₂O and Mg₃O, the dissociation energy of Mg₄O into Mg₃O and Mg is low. Mg₂O (both in the singlet and triplet states) and Mg₃O (triplet) prefer linear and planar triangular geometries, respectively. Mg₄O favors a structure only slightly distorted from planarity (*D*_{2d}) as well as a planar MgOMg₃ (*C*_s) singlet. Several additional Mg₃O and Mg₄O singlet and triplet minima are possible. (2) The high degree of Mg^{0.5-0.7+}O²⁻ ionic character as well as Mg-Mg bonding are responsible for the stability of the hypermetallated Mg₃O and Mg₄O species. However, the hyperstoichiometric Mg₂O molecule may be represented classically as Mg¹⁺O²⁻Mg¹⁺.

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Theoretical Investigation of the Geometric Structures and the Second-Order Nonlinear Optical Properties of 8-Hydroxyquinoline Derivatives

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Contribution from Hitachi Research Laboratory, Hitachi Ltd., Hitachi City, Ibaraki 319-12, Japan. Received September 4, 1991

Abstract: We report here the coupled perturbed Hartree-Fock (CPHF) ab initio extended basis set calculations on the geometric structures and static first-order (α) and second-order (β) polarizabilities of a series of 8-hydroxyquinoline molecules substituted by fluoro, chloro, nitro, and amino groups. Twenty one compounds were investigated in this study by considering the basis set dependence of the molecular hyperpolarizabilities. The effects of the nature and the position of the substituent on the geometry and the first-order and second-order polarizabilities are described. 2-Amino-6-nitro-8-quinolinol is calculated to have a β_{vec} of 14.739×10^{-30} esu which is almost twice as large as that for *p*-nitroaniline. On the basis of these calculations, new trends for the molecular design of fused heterocyclic aromatic compounds for second-order nonlinear optical applications are proposed.

I. Introduction

The discovery that conjugated organic materials exhibit large optical nonlinearities has triggered large-scale theoretical and experimental investigations in this area.¹⁻⁴ The identification of new materials with large nonlinear optical properties has many potential applications in a variety of laser-related technologies.⁴

Since most organic materials form molecular crystals in which the molecules are held by weak van der Waals interactions, their

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macroscopic properties can roughly be estimated from the microscopic properties of individual molecules. Therefore, *molecular design* has proved to be a very useful tool not only in reproducing experimental results but also in predicting nonlinear optical properties of new materials. From the theoretical viewpoint, it is believed that nonlinear optical properties of organic materials arise from microscopic hyperpolarizabilities.

Many theoretical calculations of the nonlinear optical hyperpolarizabilities have been carried out according to the electronic structures of molecular orbital theory by considering the molecular interaction with light in the Hamiltonian.⁵ Using the time dependence of the interaction Hamiltonian, the time dependent perturbation method⁶ has been widely used in the semiempirical calculations of the dynamic hyperpolarizabilities.^{5a,7} The finite field (FF) method^{1,8} in which only the static interaction Hamiltonian is utilized has been used in the ab initio calculations of static hyperpolarizabilities.^{5d} In this method the hyperpolarizability (β) components are determined by using the third-order differentiation of the energy with respect to the electric field and evaluated numerically. This numerical differentiation usually leads to large errors. Recently, however, more accurate variation perturbation methods in which the differentiation is evaluated analytically, such as the coupled perturbed Hartree-Fock (CPHF) method, have been applied for the same calculations.^{5e,9-11} This enhanced accuracy makes the CPHF method more reliable in computing static polarizabilities and hyperpolarizabilities, thus it was chosen for carrying out the theoretical calculations described here. It is worth mentioning at this point that few ab initio calculations of the nonlinear optical hyperpolarizabilities have been published, and most have dealt with relatively small molecules. In this paper we report the results of these calculations on larger systems. It is well-known that heterocyclic aromatic compounds in general and pyridine derivatives in particular offer favorable conditions for the study of the nonlinear optical effect. To the best of our knowledge, this is among the largest molecular systems thus far investigated in a systematic manner at this level of theory along with the push-pull polyene calculations reported by Soos and Ramasesha.^{12,13}

Our interest in 8-hydroxyquinoline and its derivatives came about as a result of our interest in the nonlinear optical (NLO) properties of their metal complexes. Our goal is the development of a second harmonic generation (SHG) device for use as a frequency doubler in semiconductor laser diodes. We reported earlier on the second harmonic generation properties of some metal complexes of 8-hydroxyquinoline.¹⁴ In our continued efforts to account for the origin of SHG in these materials, we undertook two parallel approaches. In the first approach we initiated a theoretical investigation to calculate the molecular hyperpolarizabilities of the ligands to identify better ligands in terms of higher NLO properties; this also serves as a first step in the calculation of the molecular hyperpolarizabilities of metal complexes. The second approach was to grow large single crystals of the most SHG active metal complexes to determine the molecular structure.

In this work we report our theoretical results on the geometric

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Table I. Basis Set Dependence of the Calculated Hyperpolarizabilities for Urea^a

basis set	β_{xxx}	β_{yyy}	β_{zzz}	$\beta_z = \beta_{xxx} + \beta_{yyy} + \beta_{zzz}$ $\times 10^{-32}$ esu
STO-3G	-32.752	5.449	15.033	-12.270
3-21G	-41.876	6.474	57.372	21.970
4-31G	-44.594	7.187	64.858	27.451
6-31G	-45.673	6.856	66.750	27.933
6-31G*	-37.984	3.283	61.668	26.967
6-31G**	-37.892	3.313	62.120	27.541

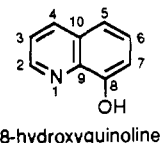
^a Observed value at 1.06 μm is 29×10^{-32} esu (ref 18).

Table II. Basis Set Dependence of the Calculated Hyperpolarizabilities for MNA^a

basis set	β_{xxx}	β_{yyy}	β_{zzz}	$\beta_z = \beta_{xxx} + \beta_{yyy} + \beta_{zzz}$ $\times 10^{-32}$ esu
STO-3G	-56.263	-5.685	461.700	399.752
4-31G	-170.632	-28.670	1129.966	930.644
6-31G	-176.546	-27.387	1152.512	938.249
6-31G*	-160.486	-22.388	994.661	801.874

^a Observed value at 1.907 μm is 950×10^{-32} esu (ref 19).

structures and the nonlinear optical properties of 8-hydroxyquinoline derivatives. The general structure of these molecules is shown below.



Twenty one compounds are thus considered: 8-hydroxyquinoline, all of its possible monosubstituted chlorine derivatives, all of its possible monosubstituted fluorine derivatives, its 2-nitro and 7-nitro derivatives, three of its amino derivatives in the 2, 6, and 7 positions, and the disubstituted 2-nitro-6-amino, 2-nitro-7-amino, and 2-amino-6-nitro derivatives.

II. Method of Calculations

All the calculations reported here have been carried out at the coupled perturbed Hartree-Fock (CPHF) ab initio level.^{15,16} For the geometry optimizations procedure, we utilized the linear combination of atomic orbitals (LCAO) Hartree-Fock energy gradient routines in the ab initio molecular orbital program Gaussian 80.¹⁷ The STO-3G basis set was used in these optimizations throughout this study. The static polarizability and hyperpolarizability tensor components have been calculated with the HONDO 7.0 set of programs.¹⁸ The α and β components are calculated *analytically* via electric field derivatives of the Hartree-Fock self consistent field (HF-SCF) total energy following a CPHF approach in which the following expansion form was used:^{15,16}

$$E = E^0 - \mu_i^0 F_i - \frac{1}{2} \alpha_{ij} F_i F_j - \frac{1}{6} \beta_{ijk} F_i F_j F_k - \dots$$

where E^0 is the unperturbed energy, F_i is the component of the field in the i direction, μ^0 is the permanent dipole moment of the molecule, and α and β are the static first-order and second-order dipole polarizability tensors.

Throughout this paper we quote the dipole moments (μ) in debye (D). The average polarizabilities (α) are expressed in cubic angstroms (\AA^3)

$$\langle \alpha \rangle = \frac{1}{3} (\alpha_{xx} + \alpha_{yy} + \alpha_{zz})$$

The β hyperpolarizabilities are expressed in terms of

$$\beta_{\text{vec}} = (\beta_x^2 + \beta_y^2 + \beta_z^2)^{1/2}$$

where

$$\beta_i = \beta_{iii} + \frac{1}{3} \sum_{j \neq i} (\beta_{ijj} + 2\beta_{jii}) \quad i, j = x, y, z$$

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Table III. Selected STO-3G Optimized Bond Lengths (Å) for Different Amino- and Nitro-Substituted 8-Quinolinsols^a

bond	H/H/H	NO ₂ /H/H	H/H/NO ₂	NH ₂ /H/H	H/NH ₂ /H	H/H/NH ₂	NO ₂ /NH ₂ /H	NO ₂ /H/NH ₂	NH ₂ /NO ₂ /H
R1	1.3167	1.3094	1.3201	1.3253	1.3163	1.3155	1.3102	1.3081	1.3291
R2	1.3989	1.3978	1.3927	1.3944	1.3962	1.4032	1.3929	1.4024	1.3900
R3	1.4448	1.4436	1.4573	1.4455	1.4443	1.4363	1.4440	1.4338	1.4507
R4	1.3629	1.3643	1.3820	1.3621	1.3605	1.3763	1.3612	1.3487	1.3608
R5	1.4199	1.4187	1.4246	1.4199	1.4303	1.4289	1.4300	1.4284	1.4190
R6	1.3896	1.3821	1.3500	1.3921	1.3885	1.4002	1.3855	1.3979	1.3892
R7		1.5176	1.4830				1.5149	1.5189	1.5057
R8				1.3994	1.4007	1.4136	1.3967	1.4109	1.3947

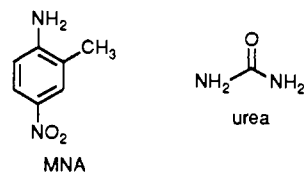
^a Bond labels and the shorthand expression X/Y/Z are the same as in Figure 1.

It is important to point out that static (zero field) hyperpolarizabilities are obtained from these calculations, while experimentally determined quantities are frequency dependent. Therefore care must be taken when comparing experimental and theoretical results. Nevertheless, our approach remains meaningful especially since we are mainly interested in comparing a series of related molecules and establishing reliable trends among them rather than attempting to predict absolute hyperpolarizability values.

III. Basis Set Dependence of the Calculated Hyperpolarizabilities

The basis set dependence of the calculated hyperpolarizabilities of urea and MNA was investigated in our group and compared with experimental data. The results are shown in Table I. Similar results have been reported by other workers.¹⁹ The molecular hyperpolarizabilities of urea and MNA were calculated by using several types of basis sets in order to examine their basis set dependence. The molecular geometries used in these calculations were optimized by using the Hartree-Fock energy gradient technique with the STO-3G basis set.

The hyperpolarizabilities were calculated by using the minimal basis set STO-3G, split valence basis sets 3-21G (for urea only), 4-31G, and 6-31G, and extended basis sets 6-31G* and 6-31G** (for urea only). The results are summarized in Tables I and II along with the experimental EFISH β values.



With the exception of STO-3G calculations, there is very good agreement between the experimental and the calculated results for both urea and MNA. The results obtained by 6-31G* and 6-31G** are not significantly different (26.967 and 27.541×10^{-30} esu respectively in the case of urea). The split valence basis sets 4-31G and 6-31G seem to be adequate for reproducing the hyperpolarizabilities. Taking into account reliability and the computational time required, the basis set 4-31G was chosen for the calculations of the hyperpolarizabilities in this study. A paper on the complete analysis of the results of the basis set dependence of the calculated static molecular hyperpolarizabilities of many well-known organic nonlinear optical materials (for which experimental values are available) is now in preparation by our group and will be published in the near future.

IV. Geometric Structures

Unlike α (which is a scalar quantity), the vector nature of β makes it very sensitive to changes in the geometrical structures. Therefore we would like to point out the importance of the geometry optimization calculations carried out for all the molecules reported here with the standard basis set STO-3G. Since the geometric changes that take place upon introducing a halogen into the parent compound (8-hydroxyquinoline) were not profound as is the case for nitro- and amino-substituted molecules, we will limit

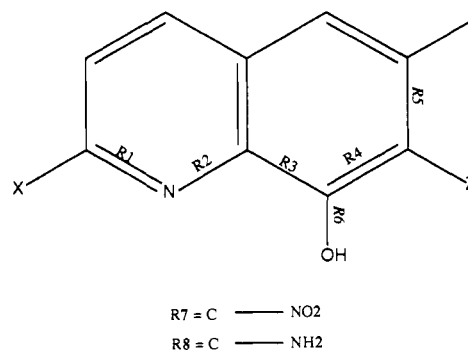


Figure 1. Structure and bond labels for the different molecules studied. The abbreviation X/Y/Z is to be used for the identification of the different derivatives.

our discussion in this section to the latter group of compounds. The shorthand format X/Y/Z shall be used from now on to refer to different compounds as shown in Figure 1. For example, NO₂/H/H stands for 2-nitro-8-hydroxyquinoline, NH₂/NO₂/H stands for 2-amino-6-nitro-8-hydroxyquinoline, and so on. Selected STO-3G optimized bond lengths of the nitro- and amino-substituted 8-quinolinol derivatives are collected in Table III. Upon substitution of 8-quinolinol, interesting trends in the evolution of the bond lengths are observed. Considering the monosubstituted derivatives we notice that the double bond character of the bonds R1, R3, and R4 in Figure 1 changes significantly depending on the position and nature of the substituents. For example, R1 (1.3167 Å) in the parent compound becomes shorter when a nitro group is introduced in the 2 position (1.3094 Å in the NO₂/H/H) and longer when an amino group is introduced in the same position (1.3253 Å in the NH₂/H/H). This trend is exalted even further in the disubstituted compound NO₂/H/NH₂ for which R1 = 1.3081 Å. If we consider the molecule NH₂/NO₂/H, we notice that R1 is the longest (1.3291 Å). Similarly R4 fluctuates from its original length in the parent compound (1.3629 Å) up to 1.3820 Å in the case of the H/H/NO₂ molecule and down to 1.3487 Å in the NO₂/H/NH₂ molecule. However, the changes in the bond lengths were not profound in the cases of R2 and R3.

Now we turn to the C---NH₂ and C---NO₂ bond lengths. In the monosubstituted compounds NO₂/H/H and NH₂/H/H the C---NO₂ and C---NH₂ bond lengths are 1.5176 and 1.3994 Å, respectively. These values become slightly smaller in the disubstituted compounds (1.5149 and 1.3967 Å in the NO₂/NH₂/H molecule).

Finally we look at the C---OH bond lengths. The C---OH bond is calculated to be 1.3896 Å in the parent compound. It becomes a little shorter when a nitro group is introduced in the 2 position (1.3821 Å), indicating more electron donating character of the OH group. An opposite trend is observed when an amino group is introduced in the same position (1.3921 Å in NH₂/H/H). This can be explained in terms of competition between two donors NH₂ and OH between which an acceptor (the nitrogen in the pyridine ring) is located. On the other hand, when an amino group is introduced into the benzene ring the role of the OH group as a donor becomes less important and thus the bond becomes longer and is calculated to be 1.4002 Å in H/H/NH₂. In total contrast, when the compound H/H/NO₂ is considered we find that the

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Table IV. Restricted Hartree-Fock (RHF) ab Initio Dipole Moments (μ), Average Polarizabilities ($\langle\alpha\rangle$), and Second-Order Polarizabilities (β_{vec}) for the Monosubstituted 8-Quinololinol Fluorine Derivatives

fluorine position	μ , D	$\langle\alpha\rangle$, Å ³	β_{vec} , 10 ⁻³⁰ esu
none	3.459	13.262	1.794
2	5.885	13.300	2.053
3	4.324	13.189	0.751
4	2.197	13.132	1.038
5	1.530	13.126	1.201
6	2.009	13.140	1.894
7	4.548	13.157	2.725

Table V. Restricted Hartree-Fock (RHF) ab Initio Dipole Moments (μ), Average Polarizabilities ($\langle\alpha\rangle$), and Second-Order Polarizabilities (β_{vec}) for the Monosubstituted 8-Quinololinol Chlorine Derivatives

chlorine position	μ , D	$\langle\alpha\rangle$, Å ³	β_{vec} , 10 ⁻³⁰ esu
none	3.459	13.262	1.794
2	5.791	14.691	2.286
3	4.368	15.881	1.110
4	2.149	14.433	0.962
5	1.447	14.404	0.861
6	1.698	15.799	2.856
7	4.314	15.539	3.438

C--OH bond length becomes rather short (1.3500 Å in the case of H/H/NO₂).

V. First- and Second-Order Polarizabilities

The Effect of Substitution Position. In order to study the effect of the substitution position on the calculated polarizabilities, we chose to calculate all the possible monosubstituted chlorine and fluorine derivatives of the parent compound, 8-quinololinol. The reason behind choosing these two halogen substituents was 2-fold: first is the relative simplicity of the computation in terms of CPU time required, and second is comparison between the two sets of compounds. The results of these calculations are shown in Tables IV and V for the fluorine and the chlorine derivatives, respectively.

If we consider the data presented in Tables IV and V we notice the following: The parent compound has a dipole moment of 3.459 D, an average polarizability of 13.262 Å³, and a β_{vec} of 1.794 × 10⁻³⁰ esu. Upon substitution the dipole moments fluctuate significantly up to 5.885 D in the case of the 2-fluoro derivative and down to 1.447 D in the case of the 5-chloro derivative, while the average polarizabilities do not change significantly. As expected, the chlorine derivatives were shown to generally have higher polarizabilities and hyperpolarizabilities. The β_{vec} values for both fluorine and chlorine derivatives substituted at the 3, 4, and 5 positions were found to be smaller than that of the parent compound (e.g. 0.861 × 10⁻³⁰ esu for the 5-chloro derivative), while those for derivatives substituted at the 2, 6, and 7 positions were found to be larger (e.g. 3.438 × 10⁻³⁰ esu for the 7-chloro derivative). 8-Hydroxyquinoline derivatives substituted with nitro and amino groups (prototypic acceptor/donor pair) at the 2, 6, and 7 positions were thus chosen for further investigation. Figure 1 shows the structure and the positions of these substituents. Table VI shows the results of the calculations.

The Effect of the Substituent. The calculated dipole moments (μ (D)), average polarizabilities ($\langle\alpha\rangle$ (Å³), and second-order polarizabilities (β_{vec} (10⁻³⁰ esu)) for the mono- and disubstituted 8-quinololinol amino and nitro derivatives are shown in Table VI. First we consider the dipole moments where monosubstitution by a nitro or an amino group increases μ (except in the case of the 2-amino derivative). The influence is greater when the acceptor is located on the pyridine ring (9.328 D for NO₂/H/H) or the donor on the benzene ring (4.673 D for H/NH₂/H). The doubly substituted molecules possess as expected the largest dipole moments in the series: $\mu = 11.276$, 10.552, and 6.629 D for NO₂/NH₂/H, NO₂/H/NH₂, and NH₂/NO₂/H, respectively.

When we turn to the average polarizabilities, we notice that all $\langle\alpha\rangle$ are within the same order of magnitude. The polariza-

Table VI. RHF ab Initio Dipole Moments (μ), Average Polarizabilities ($\langle\alpha\rangle$), and Second-Order Polarizabilities (β_{vec}) for 8-Quinololinol Derivatives Substituted at the 2, 6, and 7 Positions

X/Y/Z	μ , D	$\langle\alpha\rangle$, Å ³	β_{vec} , 10 ⁻³⁰ esu
H/H/H	3.459	13.262	1.794
F/H/H	5.885	13.300	2.053
H/F/H	2.009	13.140	1.894
H/H/F	4.548	13.157	2.725
Cl/H/H	5.791	14.691	2.286
H/Cl/H	1.698	15.799	2.856
H/H/Cl	4.314	15.539	3.438
NO ₂ /H/H	9.328	15.835	3.912
H/H/NO ₂	7.617	17.644	5.779
NH ₂ /H/H	2.626	14.414	3.645
H/NH ₂ /H	4.673	14.425	4.030
H/H/NH ₂	4.218	14.403	3.409
NO ₂ /NH ₂ /H	11.276	17.517	14.237
NO ₂ /H/NH ₂	10.552	17.120	7.308
NH ₂ /NO ₂ /H	6.629	17.550	14.739

bilities of the disubstituted molecules are almost identical: $\langle\alpha\rangle = 17.517$ Å³ for NO₂/NH₂/H and 17.550 Å³ for NH₂/NO₂/H. These values are larger than that of *p*-nitroaniline¹⁹ (10.510 Å³) and only about 30% larger than that of the unsubstituted H/H/H compound (13.262 Å³). The largest values were found for the disubstituted compound NH₂/NO₂/H (17.550 Å³).

In sharp contrast to the homogeneity of the $\langle\alpha\rangle$ values, the β_{vec} hyperpolarizabilities are scattered over almost 2 orders of magnitude. Similar differences between the first- and second-order polarizabilities in a series of analogous compounds have been reported by other researchers.²² The β_{vec} value for the unsubstituted compound H/H/H is 1.794 × 10⁻³⁰ esu which is about one-fourth of the calculated β_{vec} for *p*-nitroaniline (7.850 × 10⁻³⁰ esu) or nearly 6 times larger than that for urea (0.290 × 10⁻³⁰ esu). We would like to point out the good agreement between the calculated β_{vec} value for *p*-nitroaniline and the experimental data. This lends much confidence in our theoretical approach.

As expected, the doubly substituted NO₂/NH₂/H, NO₂/H/NH₂, and NH₂/NO₂/H molecules present larger hyperpolarizabilities, about one order of magnitude larger than that of the parent compound. NO₂/NH₂/H possesses a β_{vec} value (14.237 × 10⁻³⁰ esu) that is nearly twice as large as that of *p*-NA (7.850 × 10⁻³⁰ esu) and almost 1.5 times that of MNA. NH₂/NO₂/H possesses a β_{vec} value (14.739 × 10⁻³⁰ esu) that is similar to that of NO₂/NH₂/H. The two molecules also have similar $\langle\alpha\rangle$ values of 17.517 and 17.550 Å³ for NO₂/NH₂/H and NH₂/NO₂/H, respectively, but they have significantly different μ values, 11.276 and 6.629 D. This can be explained in terms of their molecular structures. In the case of NO₂/NH₂/H, the molecule can be viewed as composed of two parts, the electron rich benzene ring with two electron releasing groups (NH₂, OH) and the pyridine which also has two electron accepting groups (the ring's nitrogen and the nitro group). Therefore the molecule can be viewed as a linear conjugated system favoring charge transfer along its conjugation path (inter-ring charge transfer). However, in the case of NH₂/NO₂/H each of these two parts have both a donor and an acceptor group. The benzene ring has a hydroxy group and a nitro group, while the pyridine ring has an amino group as a donor and the ring's nitrogen as an acceptor. Therefore two additional intra-ring charge-transfer processes become possible in the excited state. This is probably the reason for the difference in the dipole moments of these two molecules. The fact that the molecule NH₂/NO₂/H possesses a large β_{vec} can be accounted for by considering a two-level model. The fact that the ground state dipole moment, μ , is relatively small allows for larger differences between the ground and excited state dipole moments and therefore a larger β_{vec} value. In the case of the NO₂/NH₂/H molecule the opposite is true. Large differences between the ground and the excited state dipole moments are not likely; however, the large β_{vec} calculated here is probably due to a longer

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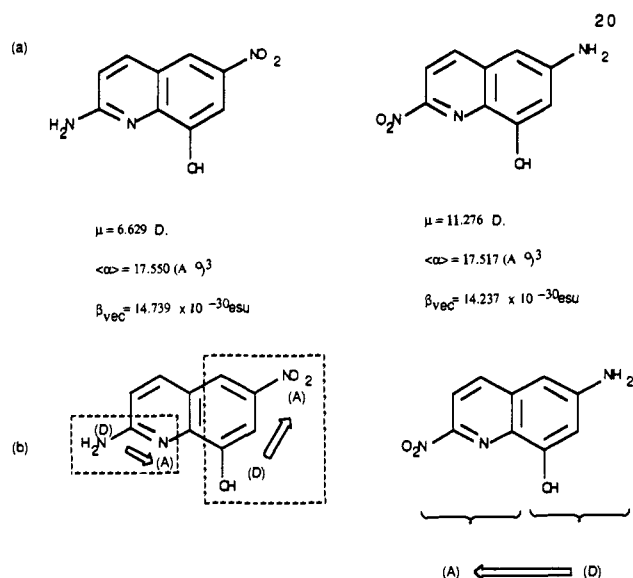


Figure 2. (a) Structures with μ , α , and β_{vec} values for the 2-amino-6-nitro-8-hydroxyquinoline and 2-nitro-6-amino-8-hydroxyquinoline molecules. (b) Sketch of the possible charge-transfer routes (denoted by the arrows) in the excited states of both molecules.

(inter-ring) conjugation path in this case. A comparison between these two molecules is shown in Figure 2.

On the basis of these findings we suggest that fused aromatic heterocyclic compounds may hold promise as potential candidates

for future nonlinear optical applications. Not only could they have reasonably large molecular hyperpolarizabilities but they also meet the optical transparency criteria required for optimizing their optical nonlinearities. As for the molecular design of new nonlinear optical materials based on quinoline or similar heterocyclic compounds, the pyridine ring can be thought of as an acceptor group within the molecule while the benzene ring can be thought of as a donor. Therefore increasing the acceptor character of the pyridine ring and/or increasing the donor character of the benzene ring would substantially increase the optical nonlinearities of this class of compounds. We also would like to point out that the nitro/amino pair is not the best acceptor/donor pair, but it was chosen in this study for the sake of simplicity and comparison.

VI. Conclusion

The coupled perturbed Hartree-Fock ab initio extended basis set calculations have been successfully applied to the calculation of the geometric structures and static first-order and second-order polarizabilities of a series of 8-hydroxyquinoline molecules substituted by halogen, nitro, and amino groups. The effects of the nature and the position of the substituent on the geometry and the first-order and second-order polarizabilities are reported. 2-Amino-6-nitro-8-hydroxyquinoline is calculated to have a β_{vec} of 14.739×10^{-30} esu which is almost twice as large as that for *p*-nitroaniline. On the basis of these calculations, new trends for the molecular design of aromatic heterocyclic compounds for nonlinear optical applications are proposed.

Calculating the β values for the mixed ligand metal complexes, in addition to the synthesis of some of the newly identified ligands and their metal complexes, and determining their SHG activities is currently underway in our laboratory.

A Theoretical Investigation of the Aluminum-Benzene Complex

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Abstract: Five optimal structures for the aluminum-benzene complex have been determined theoretically: (1) Al centered (C_{6v}), (2) Al-centered boat (C_{2v}), (3) Al on-top (C_s), (4) Al σ -bridging (C_s), and (5) Al π -bridging (C_s). Structures 4 and 2 are most likely the forms of the complex observed in low-temperature electron spin resonance (ESR) experiments. Both structures involve a boat distortion of benzene and Al σ bonds with the benzene out-of-plane para C atoms. We find little evidence for a stable Al π complex. The high-temperature Al-benzene ESR spectra can be explained by the low distortion energy for the benzene boat. Structure 3 with Al bonding on top of a single C atom is also interesting since it may be prototypical for the chemisorption interaction of an Al atom on graphite. The optimized structures were obtained from Hartree-Fock calculations using a Dunning-Hay basis set.

Introduction

The interactions between an aluminum atom and various small organic molecules have recently attracted much theoretical¹⁻³ and experimental⁴⁻¹⁰ interest. The organoaluminum σ bonds are

typically strong, and their electronic structure can often be qualitatively understood by using Hartree-Fock (HF) calculations

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