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Theoretical Investigation of the Electronic and Geometric Structures and Nonlinear Optical Properties of 2*H*-Pyrrole Derivatives

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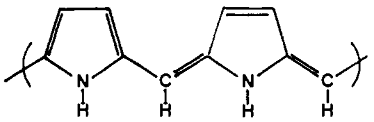
Abstract: We present Hartree–Fock ab initio extended basis set calculations on the geometric and electronic structures and static first-order (α) and second-order (β) polarizabilities of a series of 2-methylene-2*H*-pyrrole molecules, substituted by amino and nitro groups. We observe a dramatic evolution of the 2*H*-pyrrole ring geometry as a function of the nature and location of the substituent. This geometry evolution affects the first-order polarizabilities only to a very slight extent but exerts a marked influence on the second-order polarizability values, β significantly decreasing with increasing aromatic character. The 2-(nitromethylene)-5-amino-2*H*-pyrrole derivative is calculated to possess a $\beta_{\rm vec}$ value as large as that of *p*-nitroaniline.

I. Introduction

Materials exhibiting large nonlinear optical responses, in particular conjugated organic compounds, are of great importance in view of the expanding range of applications of laser technology and optical processing of information.[1-4] This has triggered numerous investigations, both from the experimental and theoretical sides, to find novel materials that could be ideally structured to suit particular second-order or third-order nonlinear optical effects.

In the search for new organic materials with potentially interesting quadratic nonlinear optical responses, low bandgap compounds can find a niche in applications such as electrooptic modulation and parametric amplification or emission. As was recently pointed out by Zyss,[5] electrooptic (Pockels) effect related applications generally qualify in this context since this effect does not generate additional optical frequencies that can get absorbed via a linear absorption mechanism. Furthermore, low bandgap materials may still be expected to satisfy the requirements for parametric amplification or emission if the first visible absorption peak is separated from the next one by a low-absorption gap allowing for the propagation of a phase-matched harmonic wave.[5]

Recently, it has been theoretically predicted that aromatic polymers can experience a strong decrease in their bandgap value when quinoid contributions to the geometry are stabilized in the ground state.[6-8] This has led Bräunling and co-workers[9] to synthesize poly(pyrrylmethine) derivatives I and II, where half the pyrrole rings (I) or all the 2*H*-pyrrole rings (II) adopt a quinoidlike conformation due to the presence of a single conjugated carbon between the rings. These polymers present bandgaps on the order of 1.0–1.5 eV, which is less than half the value in the parent polypyrrole chain (ca. 3.2 eV).[7,9]



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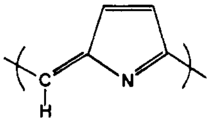
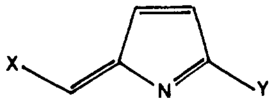


II

In this work, we report theoretical calculations on the geometric structures and the electronic and nonlinear optical properties of new charge-transfer (CT) molecules based on the repeating unit of polymer II, i.e., 2-methylene-2*H*-pyrrole. The general structure of these molecules is sketched below, where X and Y correspond to NH_2, NO_2, or H.



Seven compounds are thus considered: the unsubstituted 2-methylene-2*H*-pyrrole molecule (where both X and Y are H), which is hereafter denoted H/H, where the H on the left-hand side means X = H and the one on the right-hand side Y = H; four singly substituted compounds (where either X or Y is H and the other corresponds to NH_2 or NO_2), denoted H/NH_2 for 2-methylene-5-amino-2*H*-pyrrole, H/NO_2 for 2-methylene-5-nitro-2*H*-pyrrole, NH_2/H for 2-(aminomethylene)-2*H*-pyrrole, and NO_2/H for 2-(nitromethylene)-2*H*-pyrrole; and two doubly substituted compounds denoted NH_2/NO_2 for 2-(aminomethylene)-5-nitro-2*H*-pyrrole and NO_2/NH_2 for 2-(nitromethylene)-5-amino-2*H*-pyrrole. To the best of our knowledge, these molecules have not been synthesized yet.

It should be noted that, on the basis of experimental results, it is known that the NH_2 and NO_2 groups are not the most efficient donor and acceptor functionalities for quadratic nonlinear optics. However, they provide a very good reference point and allow direct comparisons of the hyperpolarizability components with those calculated for the *p*-nitroaniline molecule, which constitutes a prototypical push–pull organic system.

We evaluate in particular the dipole moments, the first-order polarizabilities (α), and the second-order polarizabilities (β) according to the location and the nature of the substituents. The results for the disubstituted 2-methylene-2*H*-pyrrole derivatives are compared to those obtained for related molecules and for *p*-nitroaniline.

This paper is structured as follows: In section II, we briefly outline our methodology. Sections III and IV are respectively devoted to a description of the evolutions in the geometric structures and the distributions of π-charges, as a function of substitution. The dipole moments and the α first-order and β second-order polarizabilities are discussed in section V. Our conclusions are presented in the last section.

II. Methodology

All the calculations reported here have been carried out at the restricted Hartree–Fock ab initio level with a split valence 3-21G basis set.[10] The geometry optimizations have been performed with the GAUSSIAN88 set of programs.[11] In the case of 2-methylene-2*H*-pyrrole, all the bond

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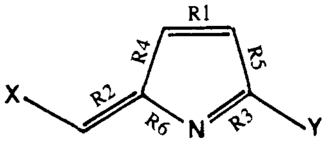
Table I. Optimized RHF/3-21G Bond Lengths (Å) for the Seven 2*H*-Pyrrole Derivatives and Corresponding Total Energies (atomic units)[a]



bond	H/H	NH_2/H	H/NO_2	NO_2/H	H/NH_2	NH_2/NO_2	NO_2/NH_2
R1	1.333	1.349	1.334	1.329	1.329	1.352	1.324
R2	1.317	1.343	1.318	1.314	1.318	1.356	1.322
R3	1.280	1.293	1.265	1.277	1.289	1.286	1.297
R4	1.479	1.450	1.477	1.485	1.489	1.446	1.499
R5	1.487	1.460	1.469	1.497	1.495	1.439	1.501
R6	1.442	1.417	1.439	1.445	1.426	1.396	1.407
E_{tot}	-245.255	-299.993	-447.539	-447.537	-299.993	-502.286	-502.289

[a] In column heads, X is on the left-hand side of the slant and Y is on the right-hand side.

lengths and angles have been fully optimized, assuming a planar geometry for the molecule. In the substituted systems, the C–H bond lengths are kept at the values optimized in 2-methylene-2*H*-pyrrole and the N–H bond lengths are set at 0.996 Å, i.e., the 3-21G-optimized value for such bonds in *p*-nitroaniline;[12] all other geometric parameters are fully optimized. We emphasize that these optimization calculations are essential to provide reliable β hyperpolarizability values since these are extremely sensitive to the details of the molecular geometries.[13]

The static polarizability and hyperpolarizability tensor components have been calculated at the RHF/3-21G level with the HONDO 8.0 set of programs,[14] on the basis of the 3-21G-optimized geometries, according to the methodology of Hurst et al.[15] The α and β components are calculated analytically via electric field derivatives of the Hartree–Fock self-consistent-field total energy, following a coupled perturbed Hartree–Fock approach:[15-17]

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

where the subscripts, which identify the tensor components, are summed over the Cartesian axes, 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.

In the rest of this paper, we quote the total dipole moments (μ) in Debye (D). The average polarizabilities $\langle\alpha\rangle$ are expressed in electrostatic units (esu) or in cubic Angstroms (Å^3) (with 1 atomic unit of first-order polarizability = 0.1482×10^{-24} esu = 0.1482 Å^3):

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

The β hyperpolarizabilities are expressed in terms of

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

$$\beta_i = \sum_j \beta_{ijj} \qquad i, j = x, y, z$$

(with 1 atomic unit of second-order polarizability = 0.8633×10^{-32} esu).

It is important to stress that Daniel and Dupuis have recently carried out an extensive study of the influence of the basis set quality on the calculated hyperpolarizability values in conjugated molecules.[18] They have found that split-valence basis sets of the 3-21G type do provide a reliable tool for the evaluation of β (whereas polarized basis sets are necessary to estimate the third-order polarizability tensor components).[18] Thus, our theoretical approach appears meaningful, especially since our main interest is in establishing reliable trends between series of molecules rather than in predicting absolute hyperpolarizability values.

III. Geometric Structures

The optimized bond lengths and the RHF/3-21G total energies for the seven 2*H*-pyrrole derivatives are collected in Table I. The unsubstituted 2-methylene-2*H*-pyrrole molecule (which corresponds to azafulvalene) presents very strong single bond and double bond characters within the five-membered ring. Taking only into account the carbon–carbon bonds, the maximum degree of bond length alternation (δ_r) is found between the methylene double bond and the ring C–C bond adjacent to it; this δr value amounts to 0.162 Å. Within the ring, the largest C–C δr value is 0.154 Å. These alternations are significantly larger than those found with the same basis set in polyene oligomers. For instance, in the case of dodecahexaene, δr is calculated to be 0.125 Å in the center of the molecule and 0.139 Å at the end of the molecule.[19] We can thus infer that there is very strong double-bond localization within the ring of the H/H molecule.

When we consider the monosubstituted derivatives, interesting trends in the evolution of the bond lengths are found (Table I). We observe two *opposite* evolutions, on the one hand, for the NH_2/H and H/NO_2 molecules and, on the other hand, for the NO_2/H and H/NH_2 molecules. In the former compounds where there is either a donor group on the methylene carbon or an acceptor group on ring position 5, there is a marked *decrease* in the degree of C–C bond length alternation, especially in the case of NH_2/H: Within the ring, the largest δr goes down to 0.111 Å for NH_2/H and 0.143 Å for H/NO_2. On the contrary, for the NO_2/H and H/NH_2 compounds, there is a marked δr *increase*: Within the ring, the largest C–C δr values are 0.168 and 0.166 Å, respectively; this enhances the double-bond localization within the rings of these molecules.

Turning to the disubstituted NH_2/NO_2 and NO_2/NH_2 compounds, we observe an *exaltation* of the trends calculated for the monosubstituted derivatives. For NH_2/NO_2, the methylene double bond becomes slightly longer (1.356 Å) than the ring C=C double bond (1.352 Å). The maximum C–C δr is found within the ring and amounts only to 0.094 Å. This value should be compared to that obtained in the fully aromatic 1*H*-pyrrole molecule at the same RHF/3-21G level: 0.074 Å. On the basis of this geometry evolution, we can conclude that the simultaneous presence of a donor group on the methylene carbon and an acceptor group on the other side of the 2*H*-pyrrole ring leads to an apparent trend toward "aromatization" of the five-membered ring.

In total contrast, in the case of the NO_2/NH_2 derivative, the ring C=C double bond becomes very short (1.324 Å) and the single bonds get very long (around 1.500 Å). This leads to a maximum ring C–C δr value of 0.177 Å, which is almost twice as large as in NH_2/NO_2. On the other hand, if we focus on the

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(11) GAUSSIAN88: Frisch, M. J.; Head-Gordon, M.; Schlegel, H. B.; Raghavachari, K.; Binkley, J. S.; Gonzalez, C.; Defrees, D. J., Fox, D. J.; Whiteside, R. A.; Seeger, R.; Melius, C. F.; Baker, J.; Martin, R.; Kahn, L. R.; Stewart, J. J. P.; Fluder, E. M.; Topiol, S.; Pople, J. A. Gaussian: Pittsburgh, PA, 1988.

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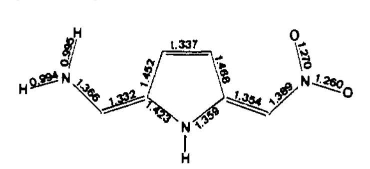
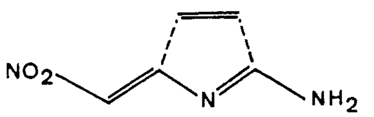


Figure 1. Optimized RHF/3-21G geometric parameters (Å and deg) for the 2-(aminomethylene)-5-(nitromethylene)pyrroline molecule.

linear carbon–nitrogen path connecting the donor and the acceptor groups, we find an average δr value of 0.082 Å. The NO_2/NH_2 molecule can thus be viewed as a linear system to which a vinylenic moiety is connected, as sketched below. We note that the C–NO_2 and C–NH_2 bond lengths are 1.434 and 1.345 Å, respectively, in the monosubstituted compounds and 1.424 and 1.329 Å in the disubstituted compounds. This slight decrease in bond length upon disubstitution is identical with that observed in *p*-nitroaniline with respect to aniline and nitrobenzene.[12]



It is interesting to note that the NH_2/NO_2 and NO_2/NH_2 isomers, even though they possess markedly different geometries, have total energies that are calculated to differ by only 1.88 kcal/mol (see Table I).

We have also studied the 2-(aminomethylene)-5-(nitromethylene)pyrroline molecule, denoted $NH_2//NO_2$. This compound corresponds to a full quinoid-type pyrrole derivative. The 3-21G fully optimized geometric parameters are presented in Figure 1. We observe that, within the ring, the maximum C–C δr value is 0.131 Å, i.e., intermediate between the corresponding values in NH_2/NO_2 and NO_2/NH_2. Our specific motivation to investigate the $NH_2//NO_2$ molecule is that full quinoid systems are known to provide large hyperpolarizabilities.[20]

IV. Charge Distributions

In order to better comprehend the dramatic geometry evolutions described in the previous section, we have investigated the π-charge distributions, as provided by a Mulliken population analysis. In view of the arbitrariness involved in such a population analysis, we are more interested in trends than in absolute charge values.

The π-charge distributions for the seven 2*H*-pyrrole derivatives are illustrated in Figure 2. In the unsubstituted H/H molecule, the ring carries a 5.09-e π-charge (electron charge units), actually stealing some π-charge from the methylene carbon, which becomes π-deficient. From this observation, we get the clue that any substituent that is able to stabilize the positive π-charge on the methylene carbon, should favor the increase of π-charge in the ring.

That this indeed occurs can be seen from a comparison of the π-charge distributions in the NH_2/H and NO_2/H compounds. In the former molecule, the mesomeric effect due to the π-lone pair of the nitrogen leads to a flux of π-charge toward the ring, which globally acquires a 5.41-e π-charge. Although this total π-charge value is still far from the 6 π-electrons required to have a full aromatic system, the trend toward "aromatization" is clear. On the opposite side, when a NO_2 group substitutes the methylene carbon, there is a flux of π-charge from the ring that only carries a 4.90-e π-charge, i.e., about 0.2 π-electron less than in the unsubstituted molecule.

The effect of monosubstitution is much weaker when the donor or acceptor group is located on ring position 5. In both cases, there is a slight increase in ring π-electron charge, the NH_2 group donating π-charge to the rest of the molecule and the NO_2 acceptor group essentially stealing π-charge from the methylene carbon.

In the disubstituted derivatives, we find a combination of the trends described above. The NH_2/NO_2 substitution leads to a total ring π-charge approaching 5.5 e. Formally, we can visualize this evolution as due to an increased contribution from the resonance form b sketched below. The NO_2/NH_2 substitution leads to a ring π-charge of 5.01 e, slightly lower than that of the unsubstituted molecule. We have also performed a full geometry optimization of the linear molecule corresponding to the conjugated path connecting the NO_2 and NH_2 groups, i.e., $NO_2CH{=}CH$-$N{=}CHNH_2$ (1-amino-4-nitro-2-aza-*trans*-1,3-butadiene) and hereafter denoted **1**. The π-charge distribution along this molecule is found to be almost identical with that of the linear segment in NO_2/NH_2. This supports the view that NO_2/NH_2 can essentially be considered as a linear extended system bridged to a vinylenic unit.

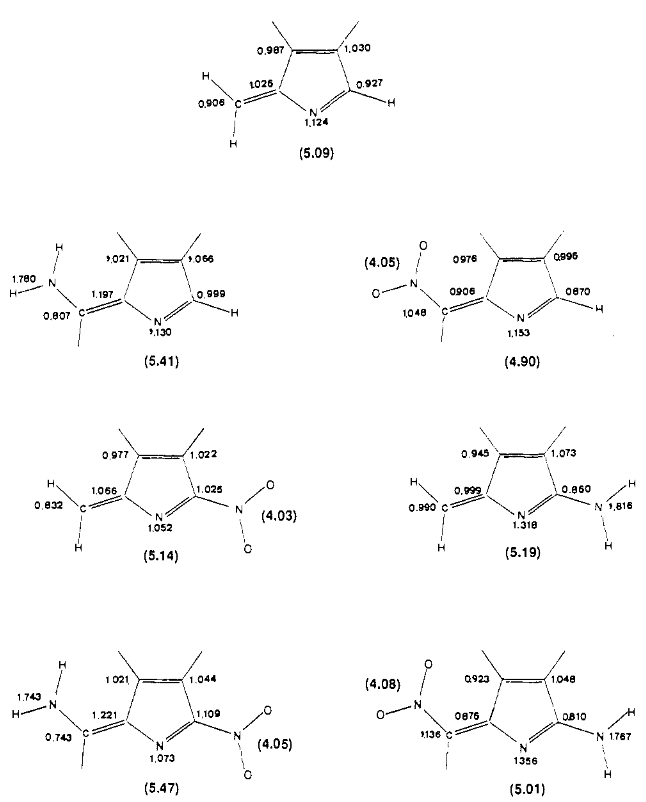
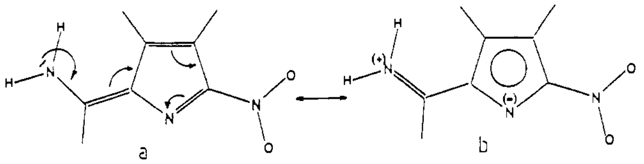


Figure 2. π-Charge distributions (electron charge unit (e)) in the 2*H*-pyrrole derivatives. The values between parentheses are the π-charges per nitro group and per cycle.



The analysis of the π-charge distribution thus confirms the conclusions drawn from the evolution of the geometric structures upon substitution. In particular, it appears that, *depending on their respective locations*, the NH_2 and NO_2 substituents influence the 2-methylene-2*H*-pyrrole system in dramatically different ways. In the next section, we investigate how these differences affect the polarizabilities of these molecules.

Another aspect that is worth mentioning is that the π-charge on the nitro groups remains very close to 4 e, even in the disubstituted molecules: 4.05 e in NH_2/NO_2 and 4.08 e in NO_2/NH_2; the latter value is identical with that in NO_2/H. These results indicate that, *in the ground state, there is no significant charge transfer from the donor group all the way to the acceptor group.* A similar conclusion has been reached from our detailed calculations on push–pull polyenes[21] and push–pull diphenylacetylenes.[12]

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Table II. RHF ab Initio Dipole Moments (μ (D)), Average First-Order Polarizabilities ($\langle\alpha\rangle$ (Å^3)), and Second-Order Polarizabilities (β_{vec} (10^{-30} esu)) for the Molecules Discussed in the Text

X	Y	μ	$\langle\alpha\rangle$	β_{vec}
H	H	2.17	7.41	0.49
NH_2	H	4.64	8.76	0.69
H	NO_2	6.69	9.35	0.21
NO_2	H	4.67	9.59	1.13
H	NH_2	2.74	10.64	2.76
NH_2	NO_2	10.98	10.99	3.06
NO_2	NH_2	7.96	11.28	7.09
molecule *1*		9.09	9.12	6.90
molecule *2*		9.38	10.12	11.33
($NH_2//NO_2$)		11.89	15.57	7.42
pNA		7.79	10.51	7.85

V. First- and Second-Order Polarizabilities

In Table II, we present the calculated total dipole moments (μ), the average first-order polarizabilities ($\langle\alpha\rangle$), and the second-order polarizabilities (β_{vec}) for the seven 2*H*-pyrrole derivatives investigated in this work. We also include in Table II the results calculated for four other molecules: (i) the 1-amino-2-aza-4-nitro-*trans*-1,3-butadiene molecule that, as pointed out above, is equivalent to the linear segment of NO_2/NH_2 and denoted **1**; (ii) the same molecule but containing only carbon atoms along the conjugated path, i.e. 1-amino-4-nitro-*trans*-1,3-butadiene, hereafter denoted **2**; (iii) the full quinoid-type pyrrole derivative $NH_2//NO_2$; and (iv) *p*-nitroaniline (denoted *p*NA), which is isoelectronic with the disubstituted 2-methylene-2*H*-pyrrole derivatives (the results for *p*-nitroaniline are taken from ref 21; similar theoretical data have also been recently reported by Itoh et al.[22]).

The dipole moment of the unsubstituted H/H molecule is already significant (2.17 D. Monosubstitution by a nitro or an amino group increases μ, the influence being greater when the donor group is located on the methylene carbon (NH_2/H; μ = 4.64 D) or the acceptor group substitutes ring position 5 (H/NO_2; μ = 6.69 D). The corresponding H/NH_2 and NO_2/H molecules have dipole moments that are about 2 D lower. The doubly substituted 2*H*-pyrrole derivatives possess as expected the largest dipole moments: μ = 10.98 and 7.96 D in NH_2/NO_2 and NO_2/NH_2, respectively. The linear molecules **1** and **2** present μ values slightly large than in NO_2/NH_2: μ = 9.09 and 9.38 D. The largest dipole moment is found for the quinoid-type system, $NH_2//NO_2$: μ = 11.89 D. We note that the dipole moment for *p*-nitroaniline is calculated to be 7.79 D, compared with an experimental value of 6.2 D in acetone.[23]

When the average first-order polarizabilities are turned to, the most striking feature is that all the $\langle\alpha\rangle$ values are of the same order of magnitude. The polarizabilities of the disubstituted molecules NH_2/NO_2 and NO_2/NH_2 are almost identical: $\langle\alpha\rangle$ = 10.99 and 11.28 Å^3; these values are very close to that in paranitroaniline (10.51 Å^3) and only about 50% larger than that in the unsubstituted H/H compound (7.41 Å^3). Once again, the largest value is found for the quinoid-type $NH_2//NO_2$ molecule: $\langle\alpha\rangle$ = 15.57 Å^3; it should be born in mind, however, that this compound contains an 8-π-electron conjugated path between the donor and acceptor groups to be compared to only a 6-π-electron unit in the 2-methylene-2*H*-pyrrole molecules.

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 first- and second-order polarizabilities in series of analogous compounds have been reported by other researchers.[13] The β_{vec} value for the unsubstituted H/H molecule is calculated to be 0.49 × 10^{-30} esu. It should be pointed out, to put this value in perspective, that despite the absence of any push–pull groups, the H/H compound has a β_{vec} that is less than 20 times lower than that calculated for *p*-nitroaniline (7.85 × 10^{-30} esu) and is nearly identical with that calculated for urea (0.48 × 10^{-30} esu).[22] We stress that the calculated β values for *p*-nitroaniline and urea are in very good agreement with the experimental data: 9.2 × 10^{-30} esu[23] and 9.6 × 10^{-30} esu[24] for *p*NA at 1.91 μm and 0.45 × 10^{-30} esu[25] for urea at 1.06 μm. This indeed lends much confidence in our theoretical approach.

Table III. Optimized AM1 Bond Lengths (Å) for 2-Methylene-2*H*-pyrrole and Its Disubstituted Derivatives (Bond Labels Are the Same as in Table I)[a]

bond	H/H	NH_2/NO_2	NO_2/NH_2
R1	1.362	1.374	1.354
R2	1.339	1.385	1.354
R3	1.314	1.344	1.355
R4	1.497	1.471	1.505
R5	1.493	1.478	1.520
R6	1.449	1.419	1.427

[a] In column heads, X is on the left-hand side of the slant and Y is on the right-hand side.

The doubly substituted NH_2/NO_2 and NO_2/NH_2 molecules, as expected, present larger hyperpolarizabilities, about 1 order of magnitude superior to that of H/H. The major results are the following.

(i) NO_2/NH_2 possesses a β_{vec} value (7.09 × 10^{-30} esu) that is very similar to, though slightly lower than, that of *p*-nitroaniline.

(ii) The NO_2/NH_2 β_{vec} value is more than twice as large as that in NH_2/NO_2, despite the fact that the two compounds possess almost identical average first-order polarizabilities. This 2-fold difference can be also traced back to the opposite characters of the two molecules, as NO_2/NH_2 can be viewed as a "linear" system (favoring charge transfer along the conjugated path) and NH_2/NO_2 as a more "aromaticlike" system. In this context, it is informative to observe that the purely linear molecule **1** possesses almost the same β_{vec} value (6.90 × 10^{-30} esu) as NO_2/NH_2. This result indicates that the vinylenic moiety present in NO_2/NH_2 to complete the 2*H*-pyrrole ring does not play any major role in the β hyperpolarizability. The difference in β_{vec} values is also pronounced in the monosubstituted molecules. The NH_2/H and H/NO_2 compounds, whose association leads to NH_2/NO_2, present β_{vec} values of the same order as the unsubstituted system H/H: 0.69 and 0.21 × 10^{-30} esu, respectively. Quite the opposite, NO_2/H and H/NH_2, the monosubstituted compounds corresponding to NO_2/NH_2, present β_{vec} values significantly larger than in H/H (see Table II). In this sense, the qualitative evolution seen in the monosubstituted compounds reflects what we observe in the doubly substituted molecules.

(iii) It is interesting to note that the dipole moments and the hyperpolarizabilities present an opposite evolution. This is in agreement with the usual concept that a compound with large β presents a large difference ($\Delta\mu$) between the ground- and excited-state dipole moments; this difference can be maximized when the ground-state dipole moment is small.

(iv) Furthermore, we observe that, when the conjugated path between the push–pull groups is made more homogeneous (for instance by going from molecule **1** to molecule **2**, which along the conjugated segment only contains carbon atoms), we obtain almost a 2-fold increase in β_{vec} (while there is hardly any change in $\langle\alpha\rangle$). The molecule **2** β_{vec} value indeed reaches 11.33 × 10^{-30} esu, which is about 40% larger than in **1**. This suggests that a similar increase could be obtained by switching from a 2*H*-pyrrole-type of ring to a 1,3-cyclopentadiene-type of ring.

(v) The quinoidlike molecule $NH_2//NO_2$, whose ring structure is a constituent of polymer I depicted in the Introduction, possesses a β_{vec} value (7.42 × 10^{-30} esu), which is intermediate between that of NO_2/NH_2 and *p*-nitroaniline. We recall, however, that $NH_2//NO_2$ contains 8 π-electrons in the conjugated path with respect to 6 π-electrons for NO_2/NH_2 and *p*-nitroaniline and appears thus on a relative basis to provide a less efficient quadratic

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Table IV. RHF/3-21G//AM1 Dipole Moments (μ (D)), Average First-Order Polarizabilities ($\langle\alpha\rangle$ (Å^3)), and Second-Order Polarizabilities (β_{vec} (10^{-30} esu)) for the Disubstituted 2-Methylene-2*H*-pyrrole Molecules

X	Y	μ	$\langle\alpha\rangle$	β_{vec}
NH_2	NO_2	11.20	11.31	2.82
NO_2	NH_2	7.93	11.50	5.61

nonlinear response than the latter two compounds.

Finally, we note that we have started to investigate the possibility of simplifying the theoretical methodology by analyzing the potentialities of an approach combining the semiempirical AM1 (Austin Model 1) technique[26] for geometry optimizations and the RHF/3-21G method for the calculations of β_{vec}. In Table III, we present the AM1-optimized bond lengths for the H/H, NO_2/NH_2, and NH_2/NO_2 compounds; all the trends found at the RHF/3-21G level (Table I) are perfectly respected within AM1, even though on the average the AM1 bond lengths are about 0.03 Å larger. The 3-21G β_{vec} values calculated on the basis of the AM1 geometries are given in Table IV for the disubstituted compounds. The results are in good agreement with the full ab initio approach, the absolute values being only slightly smaller and the relative trend being conserved. The RHF/3-21G//AM1 approach might thus prove of interest in the future.

VI. Synopsis

We have reported Hartree–Fock ab initio 3-21G calculations on the first-order and second-order polarizabilities of a series of 2-methylene-2*H*-pyrrole compounds, as well as some closely related molecules. From the discussion of our results, the following aspects can be emphasized.

Carrying out geometry optimizations (either at the ab initio or AM1 semiempirical level) on the investigated molecules is essential to obtain reliable estimates of β values. The characteristics of the push–pull compounds NH_2/NO_2 and NO_2/NH_2 turn out to be dramatically different; in the former molecule, there is a tendency toward aromatization of the 2*H*-pyrrole ring, while the latter one can be viewed as a linear system bridged by a vinylenic moiety.

The first-order α polarizabilities are calculated to be similar in all the 2*H*-pyrrole derivatives. On the contrary, the second-order β polarizabilities do differ by as much as almost 2 orders of magnitude. These results illustrate once more the important fact that trends found in first-order polarizabilities should not be blindly applied to second-order polarizabilities, whereas they can usually be extended to third-order polarizabilities with the use of appropriate scaling laws.

The unsubstituted 2-methylene-2*H*-pyrrole molecule has an intrinsically high β value, on the order of that of urea and less than 20 times smaller than that calculated for a prototypical push–pull conjugated molecule such as *p*-nitroaniline. Monosubstitution by a donor or an acceptor group leads to an evolution of β that largely depends on the nature and location of the substituent; double substitution to form a push–pull system increases β by about 1 order of magnitude.

Due to the linear character of NO_2/NH_2 versus the aromatic character of NH_2/NO_2, the β value is calculated to be 2 times larger in NO_2/NH_2 and reaches about 90% of the value calculated for *p*-nitroaniline. These results confirm that aromaticity is detrimental to the achievement of large hyperpolarizabilities.

The 2-(nitromethylene)-5-amino-2*H*-pyrrole molecule could constitute the basis of potentially interesting second-order nonlinear optical materials. Further enhancement of the nonlinear optical properties could even be envisioned by switching from a 2*H*-pyrrole type of ring to a cyclopentadiene type of ring. Indeed, a comparison of the results calculated for 1-amino-2-aza-4-nitro-*trans*-1,3-butadiene and 1-amino-4-nitro-*trans*-1,3-butadiene indicates the importance of the homogeneity of the conjugated path between the donor and acceptor groups in reaching high β values.

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