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Polarization Effects in Push−Pull Buckminsterfullerenes: A Semiempirical Study

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We predict that push−pull Buckminsterfullerenes have a high nonlinear optical response that makes pursuing their synthesis worthwhile. Three different semiempirical quantum chemical models concur to show that some isomers of push−pull C_{60} have a static first-order hyperpolarizability, β, comparable to or larger than that of *all-trans* 4-(dimethylamino)-4′-nitrodiphenyloctatetraene. Because of the geometrical structure of push−pull Buckminsterfullerenes, standard models that explain the high response in planar conjugated systems cannot be used. Rather, it is found that conjugation and inductive effects contribute at the same time to β and the separation between the nitrogen-containing groups cannot fully simulate the results of the calculations. Although these complicated materials do not easily lend themselves to simple modeling, some of the correlations of β with electronic energies, dipole moments, bond orders, and other quantities of physical interest allow us to sift through the different contributions and partially simulate the relative ordering of the hyperpolarizabilities of the various isomers. A simple perturbation approach based on icosahedral C_{60} further confirms the results obtained by the correlations and warrants the search of a topological model able to account for the response. It is found that a linear relation exists between β and the shortest resonant paths between the grafting groups. Two types of resonant structures contribute. They are described in terms of single−double bond alternation. The first resonant structure starts and finishes with hexagon-hexagon alternation (i.e., double bonds) and contributes positively, the second starts and finishes with pentagon−hexagon (i.e., single bonds) and contributes negatively. The ratio of their contributions is roughly two to one.

1. Introduction

Organic molecules are being actively investigated as candidates for new materials with the potential for molecular electronics.[1] Among their most valuable features are their structural versatility and their processability. Chemical procedures can in fact be exploited to switch on the property of interest even when this is constrained to zero, by symmetry, in the parent molecule. One such example is the group of centrosymmetric systems. In these molecules, the first-order hyperpolarizability, β, is zero. In systems with high electron mobility, introduction of push−pull groups, such as $-NH_2$ and $-NO_2$, induces large values of β. The frames of these push−pull molecules are usually polyenes and/or aromatics.

The quite flexible nature of the chemical synthesis can, however, "rig" organics with the embarrassing problem of an abundance of suitable synthetic targets. It is now becoming apparent that quantum chemistry can be of assistance in screening new materials and in gaining insight into the origin of the interactions that give rise to the response. With the advent of techniques for the gram-size production of fullerenes,[2] another class of conjugated systems is available, that is, the skeleton of C_{60} or its higher isomers. These carbon clusters are natural candidates for nonlinear optics. In the pure phase, they have been studied for their third nonlinearity,[3] while charge transfer complexes were obtained in solution to generate a sizeable second nonlinearity.[4] In the complexes, the fullerene is the electron-acceptor and the charge unbalance brings about a large polarization. Similar effects can be induced by addition of push−pull groups. Their role in fullerenes differs from the one they play in polyenes and aromatics where they substitute a hydrogen atom. In the latter compounds, the nitrogen atoms contribute to the conjugation and introduce a large asymmetry in the charge distribution. In push−pull fullerenes, the nitrogen atoms do not contribute directly to the electron conjugation but the grafting groups can still introduce a large asymmetry in the electronic wavefunction.

In this paper, we present a theoretical study at the semiempirical level of the first-order static hyperpolarizability of the 29 push−pull isomers of C_{60} in which the two nitrogen-containing groups do not interact directly. We feel that investigation of push−pull fullerenes is worth pursuing also as a study of the competition between resonance and inductive effects. We shall focus on the calculation of static β and use the results obtained in the process to attempt an analysis of the properties of these molecules.

2. Computational Background

In this work, we use two unrelated quantum chemical models to study the effect on the static hyperpolarizability of grafting an $-NH_2$ and an $-NO_2$ group to a C_{60} molecule. The rationale for this approach is not simply to compare the results, but is used because of the fact that agreement of the relative ordering of the response in the various isomers can be taken as a strong indication of the robustness of the findings. The first procedure is the sum over states, SOS, in which energies and transition dipole moments, which are obtained by diagonalization of the configuration interaction matrix, are summed to give β. The second procedure is the time dependent Hartree−Fock, TDHF, model in which the energy perturbation of the electric field of the incident radiation is expanded to second order to give β. Both methods are used at semiempirical level. The SOS model in this paper uses data obtained by the complete neglect of differential overlap/spectroscopic parameterization, CNDO/S, method.[5] In particular, the approach is based on the same configuration Interaction, CI, scheme of 14 occupied molecular orbitals and 14 unoccupied molecular orbitals that enabled us to assign the vibronic structure of the S_0−S_1 transition of C_{60}.[6] To these MOs, we add six occupied and two virtual orbitals

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mainly located at the grafting groups. Since during the study of the resonances of the third harmonic generation of C_{60}[7] we were forced to use a larger size of CI, we noticed, for a few selected molecules, that an increased CI gave similar values of β.

In practice, in the SOS scheme, the tensor element, β_{ijk}, reads

$$\beta_{ijk}(-\omega_\sigma;\omega_1,\omega_2) = 3K\left(\frac{-e^3}{\hbar^2}\right) I_{-\sigma,1,2} \sum^{ab}{}' \frac{r^k_{ga}\bar{r}^j_{ab} r^i_{bg}}{(\omega_{ab}-\omega_\sigma)(\omega_{bg}-\omega_1)} \tag{1}$$

where ω_σ is the output radiation and ω_1 and ω_2 are the perturbing radiations, which are here set to zero because we are interested in the static regime, K is a numerical factor which depends on the nonlinear phenomenon, I is an operator that permutes the indices, and r^i_{ab} is the transition dipole moment along direction i between states a and b. The bar on the top of r means that the ground state dipole moment has been subtracted, while the prime on the summation indicates the ground state is not included. Finally ω_{ab} is the energy difference between states a and b.

Throughout the paper, we shall refer to β_{tot} which reads

$$\beta_{tot} = \left(\sum_i \beta^2_i\right)^{1/2} \tag{2}$$

where

$$\beta_i = {}^1/_3 \sum_j (\beta_{ijj} + \beta_{jij} + \beta_{jji}) \tag{3}$$

In previous work, we have found the CNDO/S method to give satisfactory results for fullerenes. In particular, it allowed us to assign the vibronic structure of the S_0-S_1 transition of C_{60},[6] to assign the absolute configuration of the smallest chiral fullerene, namely C_{76}, to its circular dichroism spectrum,[8] and to assign the nature of the resonances in the third harmonic generation dispersion of C_{60} and C_{70}.[7]

The TDHF calculations were carried out with the MNDO[9] and AM1[10] methods as implemented in the MOPAC93 package.[11] Shortcomings and merits of the use of semiempirical models to evaluate nonlinear optical responses have recently been recently thoroughly reviewed.[12] Notice that another possible model, not used by us, to calculate nonlinear responses is the finite field self consistent field.[13] In principle, the three methods should give the same result for the static nonlinearities.

3. Results and Discussion

3.a. The Isomers. In principle, grafting two different groups to C_{60} gives 31 isomers. In two of them, they are attached to atoms connected by a bond so that there can be a strong interaction between $-NH_2$ and $-NO_2$, which may even result in tautomeric forms. We therefore decided to study only the 29 isomers in which the two groups are separated by at least two bonds. The isomer numbering scheme is shown in Figure 1 in the form of the Schlegel diagram of C_{60}. The bond lengths and bond angles of all the isomers were completely optimized with the MNDO semiempirical method.[9] Optimization with the related AM1 procedure[10] was deemed unnecessary since Fowler, Sandall, and co-workers have shown that for substituted fullerenes they consistently give very similar results.[14]

Upon optimization, the most significant deformations from the structure of pristine C_{60} occur in the regions of the grafting. Because of this and of the different spatial interaction between the fragment orbitals of the nitrogen containing groups and the C_{60} orbitals, one may expect that rational approaches, such as the "bond length alternation" scheme of Marder and coworkers,[15] may not succeed in rationalizing the trends of the hyperpolarizabilities.

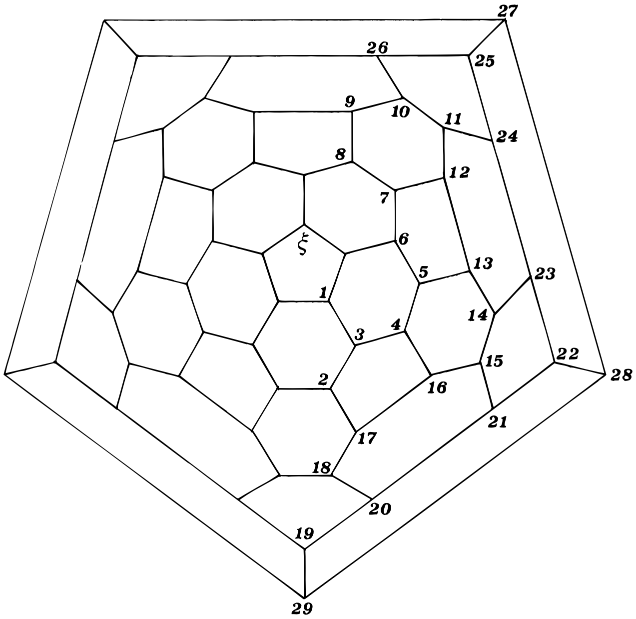

Figure 1. Schlegel representation of C_{60}. ξ refers to the position of $-NO_2$, the numbers give the positions of the $-NH_2$ groups used in the text and the tables

Inspection of the results shows that the structural parameters worth mentioning are found around the nitrogen containing groups. Two such parameters are the optimized C−N bond lengths and the optimized angles of pyramidalization at the saturated carbons. In all isomers, the two bond lengths are rather similar, with the $C-N(O_2)$ bond of the order of 1.56 Å, while the $C-N(H_2)$ bond is about 1.46 Å. This indicates that the lone pair of the $N(H_2)$ atom lends some double-bond character to the $C-N(H_2)$ bond. The pyramidalization angles at the saturated carbons are best discussed in terms of differences with respect to that of C_{60}. They tend to fall into two classes that differ by ~6°. In principle, one may expect that the smaller the angle variation the more the saturated carbon atom retains the ability to partake in the conjugation of the perturbed C_{60} frame. As such one may infer that carbon atoms attached to the amino group are more likely to show a smaller angle. Inspection of the data, also reported in the Supporting Information, confirms this conjecture.

3.b. Hyperpolarizability Results. In Table 1, we show the values of the static β for the 29 isomers of push−pull Buckminsterfullerene. They range from 0.2×10^{-29} to 44.0×10^{-29} esu in the CNDO/S calculations, from 0.3×10^{-29} to 19.8×10^{-29} esu in the AM1 calculations, and from 0.1×10^{-29} to 12.2×10^{-29} esu in the MNDO calculations. Before proceeding, and to better understand the effect of the two nitrogen-containing groups on β, these values should be compared with some external standard, possibly represented by another molecule with a large β for which experiments and calculations similar to those reported here are already available. One such instance is *all-trans* 4-(dimethylamino)-4′-nitrodiphenyloctatetraene whose SHG $\beta(-2\omega;\omega,\omega)$ was found experimentally to be 6.61×10^{-28} esu as compared with an INDO/S-SOS value of 2.56×10^{-28} esu.[16] Another comparison with other organic molecules can be made with the very extensive set of experimental results presented by Cheng et al. who screened more than 200 conjugated molecules.[17,18] In those two papers and for systems with up to 10 double bonds, the largest

TABLE 1: Calculated β, 10^{29} esu, of the 29 Push−Pull C_{60} Isomers

isomer	β(CNDO/S)	β(AM1)	β(MNDO)
1	6.850	0.478	0.371
2	3.358	0.435	0.353
3	1.078	0.446	0.379
4	4.663	0.689	0.548
5	1.580	0.468	0.396
6	9.734	0.541	0.470
7	0.216	0.337	0.280
8	11.615	0.451	0.371
9	0.768	0.541	0.366
10	1.477	0.602	0.300
11	0.741	0.525	0.311
12	4.529	0.671	0.502
13	3.711	0.495	0.304
14	3.970	0.362	0.439
15	12.070	0.716	0.763
16	7.661	1.031	0.787
17	18.276	1.308	0.291
18	8.773	0.843	0.369
19	14.259	0.603	0.100
20	15.272	2.063	4.239
21	44.023	19.846	12.210
22	14.515	2.611	2.945
23	1.292	0.508	0.264
24	11.873	4.142	5.861
25	9.735	0.439	0.254
26	6.229	1.686	0.898
27	13.901	0.346	0.918
28	4.962	0.369	0.286
29	16.104	2.599	2.734

experimental value was of the order of 2.0×10^{-28} esu. One can therefore gather that a fair number of push−pull Buckminsterfullerenes show excellent promise for a high hyperpolarizability response. Notice that, in technological applications, one may not worry about working with an isomeric mixture so long as the response of the mixture is large. It is reassuring that three different calculations present a very similar picture in which the same isomer has the highest response and that even very similar trends are observed throughout the set of 29 isomers. In particular, the AM1 and CNDO/S results show a nearly linear relation. Not surprisingly, the isomers with the largest β tend to have the two nitrogen-containing groups at the poles of the sphere. One should hasten to notice, however, that neither space separation of the nitrogens guarantees a good value of hyperpolarizability (see as a counter-example isomer **23**) nor proximity can be taken to mean that the isomer is "β silent" (see as counter-examples isomers **6** and **8**).

A further check of the robustness of the results was obtained by augmenting the size of the CNDO/S calculations for selected isomers. A 31 × 31 molecular orbital space for the CI calculations gave $\beta = 0.209 \times 10^{-29}$ esu for isomer **7**, $\beta = 40.536 \times 10^{-29}$ esu for isomer **21**, and $\beta = 12.346 \times 10^{-29}$ esu for isomer **20**. The values are quite similar to those calculated with the smaller basis of molecular orbitals so that one can conclude that the smaller basis set of molecular orbitals suffices to reach convergence for the order of magnitude of the response.

The coherent picture provided by the different types of calculations warrants further analysis. In the following, we shall focus on the CNDO/S results. Notice that, although not discussed here, correlations have also been done with AM1 or MNDO quantities which are given in the Supporting Information. The correlation between β and other quantities can be sought in several directions: the first is via mapping the values with other calculated physical quantities, such as dipole moments, energies (be they of orbitals or of electronic states) charges, bond orders, and heats of formation, which are among the obvious candidates for this kind of correlation. The second is through the use of a perturbation scheme in which the effect of the grafting groups is mimicked in a simple way. The third is by the use of topological information of C_{60}: resonance energies and bond paths are the two quantities investigated by us. The fourth possibility is to attempt to replicate the analyses performed for aromatic and polyenic push−pull molecules, be they perturbation schemes which use the interaction between fragment orbitals (see, for instance, ref 1a, pp 59 ff) or the bond alternation analysis.[15] In this last case, the perturbation analysis does not work because of the large number of states that contribute to the response (vide infra), and the Bond Alternation Analysis is not successful because the geometrical modifications induced by the grafting groups are very local and do not allow to distinguish between the various isomers.

TABLE 2: Selected CNDO/S Results: S_0 Dipole Moment, μ, D; HOMO and LUMO Energies, eV; S_1 Energy, eV; Overall Charges, q, of the $-NH_2$ and $-NO_2$ Groups

isomer	μ (D)	HOMO (eV)	LUMO (eV)	S_1 (eV)	$q(NH_2)$	$q(NO_2)$
1	5.994	−7.236	−3.429	1.246	0.535	−1.318
2	7.799	−7.353	−3.320	1.435	0.525	−1.321
3	7.128	−7.407	−3.189	1.542	0.527	−1.321
4	7.150	−7.211	−3.459	1.174	0.527	−1.321
5	7.286	−7.353	−3.176	1.531	0.525	−1.320
6	6.003	−7.121	−3.469	0.992	0.537	−1.318
7	4.914	−7.878	−2.830	2.257	0.533	−1.320
8	6.163	−7.091	−3.469	0.980	0.536	−1.321
9	6.551	−7.404	−3.184	1.564	0.526	−1.318
10	8.531	−7.363	−3.396	1.357	0.523	−1.323
11	6.606	−7.682	−3.001	1.959	0.526	−1.320
12	8.291	−7.151	−3.491	1.121	0.524	−1.323
13	6.439	−7.328	−3.323	1.448	0.527	−1.319
14	9.871	−7.208	−3.505	1.085	0.525	−1.321
15	10.574	−7.080	−3.573	0.993	0.527	−1.323
16	12.169	−7.040	−3.625	0.758	0.532	−1.324
17	10.251	−7.031	−3.581	1.000	0.527	−1.323
18	9.892	−7.138	−3.510	1.118	0.525	−1.321
19	14.105	−7.167	−3.448	1.353	0.534	−1.321
20	16.740	−6.950	−3.739	0.937	0.529	−1.321
21	14.113	−7.042	−3.649	1.309	0.536	−1.322
22	15.473	−6.942	−3.733	0.928	0.531	−1.322
23	7.563	−7.538	−3.080	1.797	0.525	−1.320
24	14.051	−7.001	−3.654	0.910	0.533	−1.322
25	8.856	−7.127	−3.497	1.157	0.526	−1.322
26	9.060	−7.211	−3.478	1.089	0.534	−1.324
27	12.197	−7.110	−3.668	0.934	0.525	−1.324
28	10.085	−7.252	−3.352	1.342	0.525	−1.320
29	17.116	−6.944	−3.750	1.058	0.538	−1.322

Two points are worth discussing: The first is that even though we have attempted to correlate β in several ways, most of which are not shown or discussed, in the end the origin of such correlations can either be traced back to the presence of the grafting groups, inductive effect, or to the presence of the C_{60} frame conjugation effect. The second is that a high degree of correlation, i.e., straight linearity, cannot be expected because of the different character of the various factors that may contribute either positively or negatively to β. It is, however, expected that a fair to good correlation can be found in certain cases.

3.c. Correlating β with Physical Quantities. In this section, we discuss the attempts to correlate β with a number of physical quantities that were chosen because of their significance. First, we examined the correlation between β (see Table 1) and the ground state dipole moments μ (see Table 2). This correlation monitors the inductive effects. Isomer **21** was found to deviate markedly from the nearly linear trend given by the remaining 28 isomers. The plot of the algebraic sum of the charges of the two grafting groups multiplied by their distance versus β was found to be very similar to that obtained with the proper dipole moments. The similarity of the two approaches implies that, so far as the hyperpolarizability is considered as only induced by the dipole moment, the C_{60} frame acts as a spacer and the inductive effects caused by the charges on the two groups govern the value of β. One can further assume that failure of isomer **21** to fall in line with the other isomers is suggestive of the presence of special inductive effects or, alternatively, of strong conjugation effects for this isomer.

Correlations between relative stabilities or the energies of the molecular orbitals and β resulted in scattered diagrams and are not discussed. However, an encouraging correlation was obtained between β and the inverse of the square of the energy of the first electronic excited state, S_1. Once again, isomer **21** played up and refused to fall in line. Because of the deviations from linearity, one can assume that the energy of the first electronically excited state, although relevant for the overall response, is not the prime responsible for it. It could be expected, in fact, that the most intense of the low-lying electronic states should give the most important contribution to β. To assess if any of the electronic states contributed most to β, we performed a missing state analysis, MSA,[19] on every isomer. In the MSA, the relative contribution τ_i of the ith state is defined as

$$\tau_i = \frac{\beta_i - \beta_T}{\beta_T} \tag{4}$$

where β_i is the value obtained excluding the ith state from all the sums and β_T is the all-state value. Unfortunately, no clear-cut, uniquely defined picture emerged from the MSA of the 29 isomers of push−pull Buckminsterfullerene. A whole range of cases is present with some molecules that owe their response to large interfering contributions while, in others, it is given by the sum of rather small positive terms. The complexity shown by the MSA indicates that the two grafting groups affect the electronic properties of C_{60} in a nonstraightforward way whose results differ greatly depending on the points of insertion.

TABLE 3: Degeneracy and Path Lengths of the Two Main Resonance Structures of Polyenes for the 29 Isomers of Push−Pull Buckminsterfullerene. Initial and Final Carbon Atoms Have the Nitrogen Attached. hh → hh: A Path That Starts with a Double Bond (Hexagon−Hexagon Edge) and Finishes with a Double Bond. ph → ph: A Path That Starts with a Single Bond (Pentagon−Hexagon Edge) and Finishes with a Single Bond

isomer	degeneracy	path length hh → hh	degeneracy	path length ph → ph
1	1	11	1	7
2	1	9	1	9
3	1	7	1	5
4	1	11	1	9
5	1	9	1	3
6	1	13	1	11
7	1	3	1	3
8	1	13	1	11
9	1	7	1	5
10	1	9	1	9
11	1	5	1	7
12	1	11	1	9
13	1	9	1	9
14	1	11	1	7
15	1	13	1	11
16	1	13	1	5
17	1	13	1	11
18	1	11	1	9
19	2	11	2	9
20	1	15	1	13
21	3	13	1	7
22	1	15	1	13
23	1	7	1	11
24	1	13	1	11
25	1	11	1	9
26	1	11	1	7
27	1	13	1	11
28	1	9	3	11
29	2	17	2	15

3.d. Correlating β by Perturbing C_{60} and by Topological Indices. The results discussed so far point towards a 2-fold nature of β in push−pull Buckminsterfullerenes. On one hand, correlation of β with the dipole moments and the charges of the grafting groups is an indication of a major role played by inductive effects. On the other hand, correlation with bond orders and electronic energies is consistent with β defined in terms of conjugation effects of the C_{60} frame. It is the interplay, and the interference, between these two mechanisms that give the large or small values of β. One may therefore wonder if the position of grafting of the two nitrogen-containing groups is of special relevance in this context. To assess this possibility, we decided to set up a calculation in which only C_{60} itself was considered. In the new set of calculations, we perturbed the icosahedral symmetry through the modification of the value of the one-electron one-center integrals $U_{\mu\mu}$ of the two atoms to which the nitrogen atoms are attached in the isomers. In one case, we added a small perturbation, δ, in the other case, we subtracted the same value, $-\delta$. This simple perturbation model gives rise to a nonzero β for C_{60}. A reasonable linearity emerged from the calculations. It was felt that this perturbation scheme is too cumbersome for general fruition and therefore we set out to find a simpler scheme able to account for the conjugative effects in terms of topological quantities which have long been recognized to be related to conjugation effects. A foremost example of such a relation is the Hückel matrix for π-electronss. When this matrix is written in units of the resonance integral, its elements are one, if two atoms are connected, and zero, if they are not. As such, it coincides with the connectivity matrix. In this model, the resonance energy is given by twice the sum of the eigenvalues of the occupied molecular orbitals minus the energy of the resonance integral multiplied by the number of atoms with π-electrons. In push−pull Buckminsterfullerenes, one can set up a similar matrix whose dimension is $60 - 2 = 58$. The two electrons that are removed are those associated with the nuclei that are attached to the nitrogens. Straight correlation of β with the resonance energies gave encouraging, although not too brilliant, results that made us believe that the topology of our systems could be used to understand the ordering of the hyperpolarizabilities in these molecules. In the end, we decided that the best way to simulate β was to focus on the two main resonance structures of polyenes. On the C_{60} surface, one can describe a very large number of paths that connect the carbons to which the nitrogens are attached. In these paths, the individual steps are either hexagon−hexagon edges, hh, or pentagon−hexagon edges, ph. The hh bonds are short and can be considered double bonds; the ph bonds are long and can be considered single bonds. If one ignores the chemical saturations, it is possible to start along the path from one of the (N)−C atoms either with a single or a double bond and continue alternating bonds until one reaches the other C-(N) atom. The path described as hh, ph, hh, ph, ..., hh is the main resonance structure of polyenes. The path described as ph, hh, ph, hh, ..., ph is their second most important resonance structure. A short program was written to calculate by brute force all these paths. In Table 3, we show the shortest path lengths for these two resonance structures with their degeneracy. Interestingly, if one plots β versus the lengths of the shortest hh → hh path multiplied by its degeneracy minus

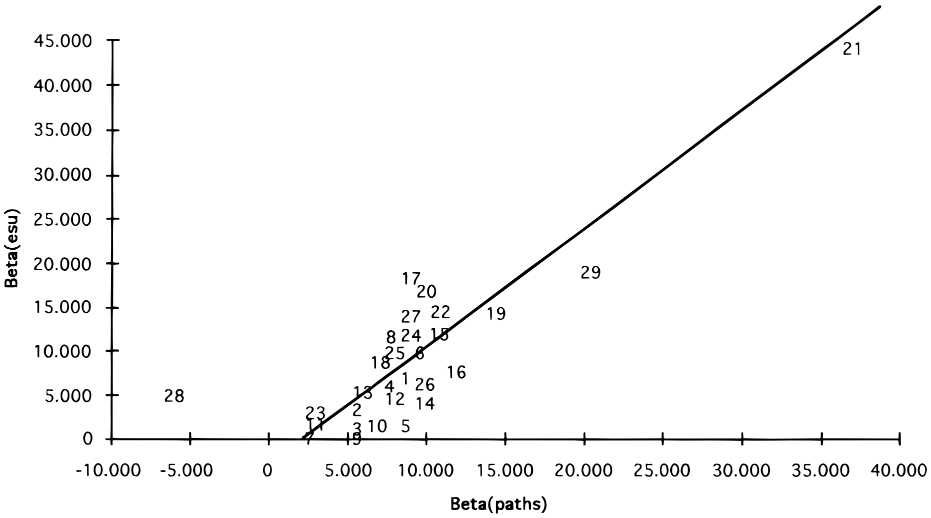

Figure 2. CNDO/S β values, esu × 10^{29}, are plotted against the corresponding values obtained as $\beta = N_{hh}L_{hh} - 0.5\ N_{ph}L_{ph}$, where N is the number of times a path is present, hh is a path described as the main resonance formula of polyenes, ph is a path described as the second resonance formula of polyenes, and L is their lengths (see text for more details and Table 3 for the figures). The position of some of the isomers labels have been shifted slightly to make them readable. The line has been added to help the eye.

one half the lengths of the shortest ph → ph path multiplied its degeneracy (see Figure 2), a quasi linear relation emerges. A fitting of the data leads to a value slightly larger than one 1.196, for the contribution of the hh → hh path and slightly smaller than one half, 0.493, for the ph → ph path. Also a non-zero constant term, 1.630, is found. Although we tend to prefer the simplicity of the equation whose results are plotted in Figure 2, it may be of consequence to try and understand if and how the result of the fitting bears on our understanding of the first order hyperpolarizability of push-pull Buckminsterfullerenes. The increased contribution of the hh → hh path with respect to the negative contributions of the ph → ph path is not overly surprising. The constant term deserves, in our opinion, some scrutiny in that it may hint that the contribution of the ph → ph is not always negative. In fact, a constant term can be introduced in the correlation by replacing the ph → ph path length by the path length minus a constant. This, in turn, indicates that there is an optimal value for this kind of path and it is the deviation from this value that gives rise to interference effects. Indeed, inspection of the results of Table 3 indicates that the minimum negative interference from the ph → ph path occurs for lengths between seven and nine bonds.

3.e. Comments on a Few Selected Isomers. In this subsection, we discuss in some detail how certain isomers fare with respect to the correlations we have presented above. Four cases are considered, they are the correlations of β with (1) μ, (2) $1/(E(S_1)^2)$, (3) β calculated for the perturbed C_{60} ($\delta = 0.5$), and (4) β calculated with the path length rule. The isomers considered are **6**, **7**, **8**, **17**, **21**, and **23**. Isomer **7** has the lowest response and is located "between" isomers 6 and 8 whose response is sizeable. Isomer **21** has the highest β while isomer **23**, which is "geographically" similar to **21**, has a very small one. Finally, isomer **17**, which for the location of the grafting groups can be described as a middle-of-the-road isomer, has the second largest calculated hyperpolarizability.

*Isomer **6**.* The major discrepancy is found for the correlation of β versus μ. In this case, the μ-derived value is less than one third than the CNDO/S value.

*Isomer **7**.* The four correlations find that this isomer should have β close to 1 unit (1 unit = 10^{-28} esu) in reasonable agreement with the full calculation.

*Isomer **8**.* The major discrepancy is found for the correlation of β versus μ. In this case, the μ-derived value is less than one third of the CNDO/S value. Slightly underestimated are the values obtained with the models based on perturbed C_{60} and the paths.

*Isomer **17**.* in absolute terms, this is one of the worst isomers for all the correlations explored. The inductive and conjugation mechanisms are likely to be strengthening each other. The dipole model underestimates β by nearly 9 units, the model based on $E(S_1)$ underestimates it by about 7 units, the perturbed C_{60} model provides an underestimate by almost 5 units, while the paths model furnishes an underestimate by some 10 units.

*Isomer **21**.* The paths model provides a good estimate of β while the others underestimate it. Dramatic breakdown is observed in the $E(S_1)$ model according to which β should be around 4 units.

*Isomer **23**.* for this isomer, the dipole-based model greatly overestimates the response by 4 units, while for the others, there is only a very slight overestimate.

Although in this section we have taken the most outstanding cases it should be clear that no model can fully account for the hyperpolarizabilities of these molecules. This should be taken as a further prove that it is the combination of conjugation and inductive effects that brings about the response in push−pull Buckminsterfullerenes. Such a combination can be constructive or destructive, for example, in isomer **17**, the two effects add to one another while in isomer **23** they interfere negatively. As mentioned above, the correlations presented should be taken more as criteria for ranking the response of the isomers and determining the order of magnitude than as strict laws obeyed by the hyperpolarizability of these molecules.

4. Conclusion

The semiempirical study, with two unrelated quantum chemical models, of 29 push−pull C_{60} isomers has shown that these molecules should absorb almost in the infrared region and should have a large nonlinear optical response comparable to that of the most active organic molecules with up to 10 double bonds. Their static first-order hyperpolarizability is spread over 2 orders of magnitude. Apart from the possible technological implications of this result, we have tried to understand the origin of the response as the combination of two effects: the first is inductive in nature and can be simulated either by the dipole moments or by the electronic charges of the $-NH_2$ and $-NO_2$ groups multiplied by the distance between their atoms. The second is related to the extensive π-electron system of C_{60}: grafting of the push−pull groups decreases the conjugation. It may not come as a surprise that the smaller the bond order between the carbons and the nitrogens the greater the participation of the carbon atoms to the π-framework and the larger the response. Nor may it be unexpected that the inverse of the square of the energies of the first excited state can correlate with the hyperpolarizabilities.

To further understand the contributions of the fullerenic frame, we have used two simple models. In the first, the semiempirical quantum chemical calculation simulates the effects of the two nitrogen-containing groups through the perturbation of the one-centre one-electron integrals of icosahedral C_{60}. In the second, the two most important resonance structures of push−pull polyenes are sought out for every isomer and their lengths are found proportional to β.

Inspection of the results obtained by correlation of β with the four models shows that inductive and conjugation contributions may add or subtract. Interestingly, some of the models used can simulate the very large hyperpolarizability of isomer **21** and the very small one of isomer **23**. In these two isomers, the positions of the two nitrogen-containing groups are very similar and they are located at the poles of the sphere. They can also reproduce the similar hyperpolarizabilities shown by isomers **6** and **8**, which have a large response, and the small response of isomer **7**, which is geographically similar to them.

We would like to conclude by mentioning that extension of this work may be possible in more general terms: for instance, although the theory of multiple additions to C_{60} is still in its infancy, one may hope that simple modeling based on resonance structures, such as that used here, will be developed and will yield a rationalization of the high selectivity observed experimentally.

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Supporting Information Available: Four tables including a listing of selected optimized structural parameters, the MNDO and AM1 counterparts of Table 2, and the β values obtained perturbing the electronic structure of pristine C_{60} (4 pages). Ordering information is given on any masthead page.

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