Linear Molecular-mass Dependence of Second Hyperpolarizabilities: Lack of Polar Enhancement in Nonconjugated Molecules

Daniel Kost,[b] Alan T. Yeates[a] and Douglas S. Dudis[a]

[a] *US Air Force Materials Laboratory, Polymer Branch, Wright-Patterson AFB, OH 45433, USA*
[b] *Department of Chemistry, Ben-Gurion University of the Negev, Beer Sheva 84105, Israel*

Second hyperpolarizabilities (γ) of a series of R–X molecules (R = H, Me, Et, Pr^i, Bu^t; X = –NCHO, OH, Me) have been calculated at various *ab initio* levels; surprisingly, γ increases nearly linearly with molecular mass, is minimally affected by the functional group X, and is slightly greater for alkanes.

In the study of materials with large nonlinear optical (NLO) activities to be utilized in future technologies, it is of paramount importance to understand the relationship between molecular structure and NLO properties.[1] Computational chemistry has been useful for this purpose, in an attempt to design and suggest potential target molecules for preparation and further screening. This is so because many of the fast (femtosecond) NLO experiments measure primarily molecular electronic responses, as opposed to thermal and other bulk effects. The object of the present work is to systematically study inductive effects of alkyl groups on NLO properties of *N*-alkylformamides **1**, in response to observations that suggested such effects might enhance γ in simple molecules with formal charge-transfer character in the ground state.[2]

It was speculated that the increasing electron release by alkyl groups in the series H < Me < Et < Pr^i < Bu^t might stabilize the polar contribution to the amide structure, **2**, and cause enhancement of γ. To provide a frame of reference, two other series of compounds were also calculated: the nonpolar alkanes **3**, in order to measure simple molecular mass effects; and the polar alcohols **4**, in order to ascertain the alkyl substituent effect on molecules with permanent dipole but no resonance itneractions leading to charge transfer states.

Ab initio calculations were performed using the GAUSSIAN90[3] system for geometry optimizations and the GAMESS[4] program. The geometries of all molecules were fully optimized at the RHF/6-31G* level. NLO properties were calculated using the finite field (derivative) method,[5] as implemented in the GAMESS program, at the 6-31G* optimized geometries, using two basis sets: 6-31G*, and 6-31G* to which diffuse p and d functions (ζ = 0.05)[6] had been added for all C, N and O atoms. This basis set is noted as 'diffuse'. Neither polarization nor diffuse functions were used for hydrogen atoms, for it had been found that such functions had no significant effect on resulting second hyperpolarizability.[7] The NLO properties reported here are all orientationally averaged quantities, calculated from the individual tensor components.[5]

Fig. 1 presents the second hyperpolarizabilities, calculated at both basis sets. Examination of Fig. 1 reveals first a dramatic basis set effect: γ-values obtained using the diffuse basis set are five- to ten-fold greater than the corresponding values at the 6-31G* level. This confirms earlier observations in conjugated systems, concering the importance of diffuse functions in properly describing γ.[6] The second result arising from Fig. 1 is that in all three compound series, γ increases uniformly with increasing number of carbons in the alkyl skeleton. This suggested that γ increased primarily as a function of molecular mass. Indeed, a plot of γ against MM (Fig. 2) yielded reasonably straight lines for each basis set, accommodating both the amide and the alcohol series on the same lines (correlation coefficients: 0.994 and 0.988 for the 6-31G* and the diffuse basis set results, respectively). The alkane series also follows the same general trend, except that the points representing these nonpolar compounds consistently show positive deviation from the lines. These remarkable observations lead to the following conclusions: (*a*) no special inductive effect of the alkyl groups operates on the polarizable formamides, as roughly the same slope is found for all three series of compounds, including the nonpolar alkanes; (*b*) even more surprising, the magnitude of γ does not change significantly from one series to another, *i.e.* it is essentially immaterial which functional group is present; (*c*) if any functional-group effect can be found, it is a small but distinct decrease in γ in the presence of the polar groups, relative to the alkane series.

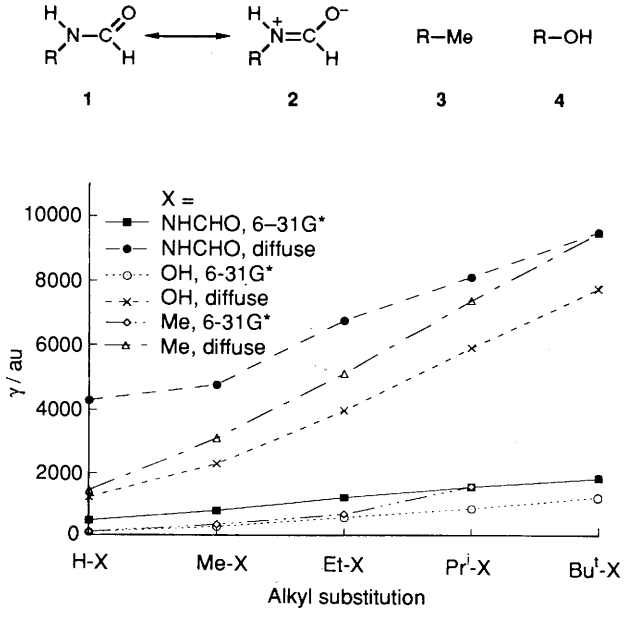

Fig. 1 Calculated second hyperpolarizabilities for series **1**, **3** and **4** plotted against the size of the alkyl substituent; units are atomic units

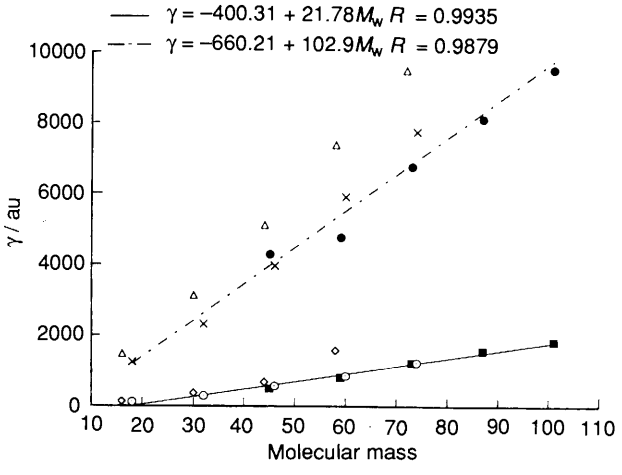

Fig. 2 Calculated second hyperpolarizabilities for series **1**, **3** and **4** plotted against molecular mass. The lines represent linear least-squares fits for both the alcohol and amide series, at the 6-31G* level (——) and at the diffuse basis (– – –). The legend for data points is the same as in Fig. 1.

The evident absence of, or even negative effect of polar groups is particularly troubling, in view of reports suggesting that polar functional groups lead to larger γ.† The present study indicates that in the small molecules studied, polar groups had no enhancing effect on γ. Quite to the contrary, for a given molecular mass, the alkane series tends to have a greater γ than any one of the formamide and alcohol series. To accommodate this apparent conflict between the present data and former experiments, it may be argued that polar groups generate large γ-values only as long as they are associated with extended conjugated systems. Alternatively, this effect may only be manifest at post Hartree–Fock theories. Further work addressing this problem is underway.

D. K. thanks the National Research Council (NRC) and the Air Force Systems Command (AFSC) for the award of an NRC Research Associateship.

Received, 27th July 1992; Com. 2/04019K

† *Cf.* for instance, Fig. 4 in ref. 1(*a*).

References

1 For reviews on NLO materials see: (*a*) P. N. Prasad and B. A. Reinhardt, *Chem. Mater.*, 1990, **2**, 660; (*b*) *Nonlinear Optical Properties of Organic and Polymeric Materials*, ed. D. J. Williams, ACS Symp. Ser. 233, A.C.S., Washington DC, 1985; (*c*) *Nonlinear Optical Properties of Organic Molecules and Crystals*, ed. D. S. Chemla and J. Zyss, Academic, Orlando 1987, vols. I and II.
2 D. Spangler, personal communciation; B. A. Reinhardt, unpublished results.
3 M. J. Frisch, M. Head-Gordon, G. W. Trucks, J. B. Foresman, H. B. Schlegel, K. Raghavachari, M. A. Robb, J. S. Binkley, C. Gonzalez, D. J. Defrees, D. J. Fox, R. A. Whiteside, R. Seeger, C. F. Melius, J. Baker, R. L. Martin, L. R. Kahn, J. J. P. Stewart, S. Topiol and J. A. Pople, GAUSSIAN90; Gaussian, Inc., Pittsburgh PA, 1990.
4 M. W. Schmidt, K. K. Baldridge, J. A. Boatz, J. H. Jensen, S. Koseki, M. S. Gordon, K. A. Nguyen, T. L. Windus and S. T. Elbert, *QCPE Bull.*, 1990, **10**, 52.
5 H. A. Kurtz, J. J. P. Stewart and K. M. Dieter, *J. Comp. Chem.*, 1990, **11**, 82.
6 G. J. B. Hurst, M. Dupuis and E. Clementi, *J. Chem. Phys.*, 1988, **89**, 385.
7 J. Bloor, personal communication.