Inorg. Chem. **1993**, *32*, 277–280

Interpretation of the Second Hyperpolarizability of $Ni(S_2C_2H_2)_2$ and Some of Its Derivatives. A Comparative Study

M. G. Papadopoulos* and J. Waite*

National Hellenic Research Foundation, 48, Vas. Constantinou Avenue, Athens 116 35, Greece

C. S. Winter and S. N. Oliver

British Telecom Research Laboratories, RT2333, Martlesham Heath, Ipswich IP5 7RE, United Kingdom

Received April 10, 1992

The second hyperpolarizability, γ, of $Ni(S_2C_2H_2)_2$ (NiBDT) and some of its methyl derivatives has been computed using a well-tested semiempirical approach. The necessity of 3d functions for sulfur on the computation of γ has been documented. The factors which affect the large hyperpolarizability of NiBDT are discussed, and the contributions of the metal on the nonlinearities are commented on by considering some fragments of NiBDT and the nonlinearity of tetrathiafulvalene. The *trans*-dimethyl derivative of NiBDT is shown to have a very large γ value. The anisotropic structure of the considered molecules has been analyzed using the ratios $\gamma_{zzzz}/\gamma_{xxxx}$ and $\gamma_{zzzz}/\gamma_{yyyy}$. The polarizabilities of the studied organometallics are also presented.

I. Introduction

There is currently an increasing interest in the design and synthesis of materials with optimized properties for specific uses.[1] Among these, one may note nonlinear optics, where there is a large number of applications (e.g. telecommunications, optical information processing, etc.)[2] requiring such materials. Very often one wants to maximize $\chi^{(3)}$ (the macroscopic, third-order susceptibility), which is related to the second order hyperpolarizability, γ,[3,4] and many organic molecules have been tried (theoretically and experimentally) in order to fulfill this requirement.

Recently, organometallics have started to attract the interest of researchers in this field,[5] since many of these have low-lying excited states and thus are likely to be associated with large hyperpolarizabilities. References 5a–f denote experimental works while refs 5g–i are theoretical studies. In the latter Kanis et al.[5i] reported the first hyperpolarizability (computed using the ZINDO method) of several derivatives involving some interesting metal–organic chromophores. A highly promising class of organometallic compounds, for making simple all optical switching devices is that of the dithiolene derivatives.[6a] Among these which have already been studied are $Ni(S_2C_2R_2)_2$, where R = CH_3, C_2H_5, or C_6H_5, employing the degenerate four-wave mixing technique.[6b,c] These experiments were aiming at exploiting the near-resonance phenomena in order to produce materials for devices in nonlinear optics, working in the picosecond range.[6b,c] Thus, it was considered useful to employ a simple but well-tested theoretical method to comment on and clarify the structure–polarization relationship of these interesting organometallic compounds.

More specifically, the question of whether 3d orbitals on sulfur are required for the present semiempirical computations was addressed. Subsequently considerable care was exercised to develop the appropriate basis sets that were both flexible enough and compact. Having tackled the above methodological problems we proceeded to connect the hyperpolarizability of $Ni(S_2C_2H_2)_2$ [bis(ethylene-1,2-dithiolato)nickel] or NiBDT, with its electronic structure and interpret it (Figure 1a). The charge transfer (CT) from Ni to the ligands and the extensively delocalized π electrons have been used to rationalize the results.

Furthermore, insight into the role of the metal is gained by analyzing the properties of some relevant fragments of NiBDT and by comparing its effect with that which is produced by replacing Ni with C=C (this is the bridging bond in tetrathi-

---

(1) (a) Hutchings, M. G.; Gordon, P. F.; Morley, J. O. *Materials for Non-Linear and Electro-Optics 1989, Proceedings of the International Conference, Cambridge, England*; Institute of Physics: Bristol, England, 1989; p 97. (b) Groh, W.; Lupo, D.; Sixl, H. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1548. (c) Aakeroy, C. B.; Hitchcock, B. P.; Moyle, B. D.; Seddon, K. R. *J. Chem. Soc., Chem. Commun.* **1989**, 1856. (d) Li, DeQuan; Ratner, M. A.; Marks, T. J. *J. Am. Chem. Soc.* **1990**, *112*, 7389. (e) Ulman, A.; Willand, C. S.; Köhler, W.; Robello, D. R.; Williams, D. J.; Handley, L. *J. Am. Chem. Soc.* **1990**, *112*, 7083.

(2) Williams, D. J., Ed. *Non-Linear Optical Properties of Organic and Polymeric Materials*; American Chemical Society: Washington, DC, 1983.

(3) (a) Sohn, J. E.; Singer, K. D.; Kuzyk, M. G.; Holland, W. R.; Katz, H. E.; Dirk, C. W.; Schilling, M. L.; Comizzoli, R. B. *Non-Linear Optical Effects in Organic Polymers*; Messier, J., Kajzar, F., Prasad, P., Ulrich, D., Eds.; NATO ASI Series 162, Kluwer Academic Publishers: London, 1988; p 291. (b) Levine, B. F.; Bethea, C. G. *J. Chem. Phys.* **1975**, *63*, 2666.

(4) (a) The mean second hyperpolarizability, γ, is given in refs 4b,c as

$$\gamma = (1/5)(\gamma_{xxxx} + \gamma_{yyyy} + \gamma_{zzzz} + 2\gamma_{xxzz} + 2\gamma_{yyzz} + 2\gamma_{xxyy})$$

where the suffixes x, y, and z denote Cartesian components. (b) Bogaard, M. P.; Orr, B. J. *Physical Chemistry, Series Two*, Vol. 2, Buckingham, A. D., Ed.; MTP International Review of Science: Butterworths: London, 1975; Vol. 2, p 149. (c) Buckingham, A. D.; Orr, B. J. *Q. Rev. Chem. Soc.* **1967**, *21*, 195.

(5) (a) Tam, W.; Eaton, D. F.; Calabrese, J. C.; Williams, I. D.; Wang, Y.; Anderson, A. G. *Chem. Mater.* **1989**, *1*, 128. (b) Tam, W.; Guerin, B.; Calabrese, J. C.; Stevenson, S. H. *Chem. Phys. Lett.* **1989**, *154*, 93. (c) Tam, W.; Calabrese, J. C. *Chem. Phys. Lett.* **1988**, *144*, 79. (d) Winter, C. S.; Oliver, S. N.; Rush, J. D. *Non-Linear Optical Effects in Organic Polymers*; Messier, J., Kajzar, F., Prasad, P., Ulrich, U., Eds.; NATO ASI Series 162; Kluwer Academic Publishers: London, 1988; p 247. (e) Winter, C. S.; Oliver, S. N.; Rush, J. D. *Opt. Commun.* **1988**, *69*, 45. (f) Ghosal, S.; Samoc, M.; Prasad, P. N.; Tufariello, J. J. *J. Phys. Chem.* **1990**, *94*, 2847. (g) Waite, J.; Papadopoulos, M. G. *Z. Naturforsch.* **1987**, *42A*, 749. (h) Waite, J.; Papadopoulos, M. G. *J. Phys. Chem.* **1991**, *95*, 5426. (i) Kanis, D. R.; Ratner, M. A.; Marks, T. J. *J. Am. Chem. Soc.* **1990**, *112*, 8203.

(6) (a) Calvert, P. *Nature* **1991**, *350*, 114. (b) Oliver, S. N.; Winter, C. S.; Rush, J. D.; Underhill, A. E.; Hill, C. *Proc. SPIE-Int. Soc. Opt. Eng.* **1990**, *1337*, 81–8. (c) Winter, C. S.; Hill, C.; Underhill, A. *Appl. Phys. Lett.* **1991**, *58*, 107. (d) The average polarizability α is given by

$$\alpha = (1/3)(\alpha_{xx} + \alpha_{yy} + \alpha_{zz})$$

where the subscriptes x, y, and z denote Cartesian components.

0020-1669/93/1332-0277$04.00/0

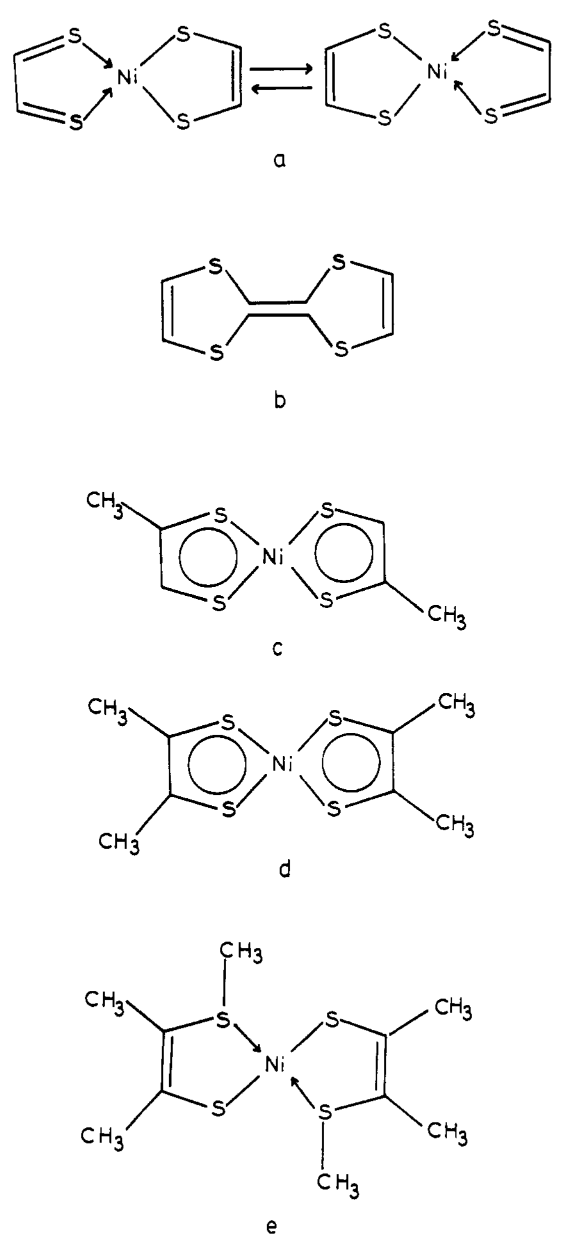

Figure 1. Structures of (a) NiBDT, (b) TTF, (c) $H(CH_3)C_2S_2NiS_2C_2H_2(CH_3)H$, (d) $Ni[S_2C_2(CH_3)_2]_2$, and (e) $Ni[(CH_3)_2S_4C_4(CH_3)_4]$. Information for the coordinate system is given in footnote *a* of Table I.

afulvalene, TTF). It is also shown that substitution (and use of the appropriate functional groups) is a powerful means for fine tuning the hyperpolarizability. This point is demonstrated by the successive methylation of NiBDT. The present study is facilitated by comparing certain trends in the hyperpolarizability results with the corresponding ones in the polarizability values.[6d]

II. Computational Method

The presented results have been computed employing the CHF-PT-EB-CNDO method.[7] This technique relies on an extended basis CNDO wave function (EB-CNDO),[8] which is perturbed using McWeeny et al.'s coupled Hartree-Fock perturbation theory.[9] This semiempirical approach uses basis sets which are optimized with respect to the polarizability and/or the second hyperpolarizability of a few carefully selected model compounds. The so derived set of atomic functions are subsequently employed for the computation of the properties (α, γ) in a series of structurally similar compounds. This particular feature allows the property values and even more the trends to be described reasonably well.[7,10]

The rigorous computation of static molecular hyperpolarizabilities requires very large basis sets (with adequate polarization and diffuse functions) and satisfactory treatment of correlation, as well as of vibrational contributions. Such calculations for most molecules of chemical interest require computing facilities not easily available. Thus, elaborate computations of the molecular second hyperpolarizability are performed only on small molecules (e.g. di- and triatomics).[11] However, it has been established that simple, approximate theories may give valuable information for basic trends, significant mechanisms of polarization and the recognition of those bonding patterns which are likely to produce unusual electric properties.[7,10] Such a model is employed in the present work.[7,10] This heavily relies on the quality of the basis sets, and thus we comment on the functions used for the presented computations.

For HC≡CH the following orbitals have been employed:

C: 2s,p (1.3)

H: 1s (0.75); 2s,p (0.397)

This basis was optimized for C_6H_8 (1,3,5-trans-hexatriene). It gave $\gamma = 90\,000$ au, while the corresponding experimental value is $89\,700 \pm 8340$ au.[12a,b]

For S, the functions

3s,p (1.2); 3d (0.348)

have been used. These were optimized with respect to the polarizability of CS_2. For C the above-defined functions have been employed. This basis gave, for CS_2, $\alpha = 59.8$ au, while the experimental values for α are 61.0 (at 488.0 nm), 60.4 (at 514.5 nm), and 58.5 au (at 632.8 nm).[12c]

For CH_3 the following functions have been used:

C: 2s,p (1.625)

H: 1s (0.939); 2s,p (0.46)

These orbitals gave, for the polarizability and second hyperpolarizability of CH_4, $\alpha = 17.5$ au and $\gamma = 2890$ au. The experimental values are $\alpha = 17.55$ au[12d] and $\gamma = 2890$ au.[12e]

We shall now discuss whether it is necessary to use 3d functions on sulfur, so that the computed results are reasonable and consistent. In a recent work on α and γ of some substituted polythiophenes, we found that: "if d orbitals are not used for sulfur the polarizability is smaller (on average by 8.9%), while the second hyperpolarizability is larger (on average by 8.5%) in comparison to the results produced by the basis which included d functions."[10b]

Herman et al.[12f] have studied, (employing INDO-type LCAO CI calculations), the role of 3d(S) orbitals on some properties (e.g. nature

---

(7) (a) Nicolaides, C. A.; Papadopoulos, M. G.; Waite, J. *Theor. Chim. Acta* **1982**, *61*, 427. (b) Papadopoulos, M. G.; Waite, J.; Nicolaides, C. A. *J. Chem. Phys.* **1982**, *77*, 2527. (c) Waite, J.; Papadopoulos, M. G.; Nicolaides, C. A. *J. Chem. Phys.* **1982**, *77*, 2536. (d) Waite, J.; Papadopoulos, M. G. *J. Chem. Phys.* **1985**, *82*, 1427. (e) Papadopoulos, M. G.; Waite, J. *J. Chem. Phys.* **1985**, *82*, 1435. (f) Waite, J.; Papadopoulos, M. G. *J. Chem. Phys.* **1985**, *83*, 4047. (g) Waite, J.; Papadopoulos, M. G. *J. Chem. Phys.* **1990**, *94*, 1755.

(8) Pople, J. A.; Beveridge, D. L. *Approximate Molecular Orbital Theory*; McGraw-Hill, New York, 1970.

(9) McWeeny, R. *Phys. Rev.* **1962**, *126*, 1028. Diercksen, G.; McWeeny, R. *J. Chem. Phys.* **1966**, *44*, 3554. Dodds, J. L.; McWeeny, R.; Raynes, W. T.; Riley, J. P. *Mol. Phys.* **1977**, *33*, 611.

(10) (a) Papadopoulos, M. G.; Waite, J. *J. Chem. Soc., Faraday Trans.* **1990**, *86*, 3525. (b) Waite, J.; Papadopoulos, M. G. *J. Phys. Chem.* **1990**, *94*, 6244. (c) Waite, J.; Papadopoulos, M. G. *J. Phys. Chem.* **1989**, *93*, 43. (d) Papadopoulos, M. G.; Waite, J. *J. Chem. Soc., Faraday Trans.* **1989**, *85*, 1885.

(11) (a) Sekino, H.; Bartlett, R. J. *J. Chem. Phys.* **1986**, *84*, 2726. (b) Maroulis, G.; Thakkar, A. J. *J. Chem. Phys.* **1990**, *93*, 4164. (c) Bishop, D. M.; Pipin, J. *J. Chem. Phys.* **1989**, *91*, 3549. (d) Jaszunski, M.; Roos, B. O. *Mol. Phys.* **1984**, *52*, 1209.

(12) (a) Ward, J. F.; Elliott, D. S. *J. Chem. Phys.* **1978**, *69*, 5438. (b) The experimental measurement has been performed by using a gas in which the cis isomer is 10–40% and the trans 90–60%.[12a] The method was the dc electric-field induced optical second harmonic generation. (c) Bogaard, M. R.; Buckingham, A. D.; Pierens, R. K.; White, A. H. *Trans. Faraday Soc.* **1978**, *74*, 3008. (d) Shinoda, H.; Akutagawa, T. *Bull. Chem. Soc. Jpn.* **1975**, *48*, 3431. (e) Buckingham, A. D.; Orr, B. J. *Trans. Faraday Soc.* *65*, 673 (1969). (f) Herman, Z. S.; Kirchner, R. F.; Loew, G. H.; Muller-Westerhoff, U. T.; Nazzal, A.; Zerner, M. C. *Inorg. Chem.* **1982**, *21*, 46.

Table I. The Second Hyperpolarizability, γ,[a] and the Anisotropies γ_1 and γ_2 of NBDT, Some of Its Methyl Derivatives and Fragments[b] (Properties of TTF Included for Comparative Purposes)

compound		S(3s3p3d)[c]			S(3s3p)[d]
no.	formula	γ_1	γ_2	γ	γ
1	$Ni(S_2C_2H_2)_2$	11.8	4.11	397 000	722 000
2	$S_2C_2H_2$	14.6	0.82	17 700	
3	$NiS_2C_2H_2$	12.4	1.73	81 500	119 000
4	TTF	−11.1	3.64	250 000	
5	$H(CH_3)C_2S_2NiS_2C_2(CH_3)H$	23.4	6.60	983 000	nc[e]
6	$[H(CH_3)C_2S_2NiS_2C_2(CH_3)H]^{2-}$	24.3	13.7	3 780 000	
7	$Ni[S_2C_2(CH_3)_2]_2$	3.94	2.45	628 000	747 000
8	$Ni[(CH_3)_2S_4C_4(CH_3)_4]$			812 000	1 010 000

[a] 1 au of second hyperpolarizability $\simeq 0.503717 \times 10^{-39}$ esu $\simeq 0.623597 \times 10^{-64}$ C^4 m^4 J^{-3}. [b] Geometric data for the coordinates have been taken from refs 24 and 25. For the specification of the molecular coordinates, it is noted that the NiS_4C_4 plane coincides with that defined by *yz* and the *z* axis is perpendicular to the carbon–carbon bond of the S_2C_2 group. The anisotropies of $Ni[(CH_3)_2S_4C_4(CH_3)_2]_2$ (Table I) have not been considered, since the NiS_4 plane does not coincide with *yz*, because the compound has been rotated so that its dipole moment coincides with the *z* axis. Thus, the anisotropies of this molecule are not easily comparable with those presented in Table I. The coordinates of the molecules which are studied in this work are available on request. [c] S: 3s(3.0), 3p(3.0), 3d(1.0). [d] S: 3s(3.0), 3p(3.0). [e] The first-order correction to the density matrix did not converge.

Table II. Polarizability of NiBDT and Some of Its Methyl Derivatives

compound		α[a]	
no.	formula	S(3s3p3d)	S(3s3p)
1	$Ni(S_2C_2H_2)_2$	288	314
2	$S_2C_2H_2$	84.3	
3	$NiS_2C_2H_2$	110	90.3
4	TTF	215	
5	$H(CH_3)C_2S_2NiS_2C_2(CH_3)H$	364	nc[b]
6	$[H(CH_3)C_2S_2NiS_2C_2(CH_3)H]^{2-}$	588	
7	$Ni[S_2C_2(CH_3)_2]_2$	379	346
8	$Ni[(CH_3)_2S_4C_4(CH_3)_4]$	424	392

[a] 1 au of polarizability $\cong 0.148176 \times 10^{-24}$esu $\cong 0.164867 \times 10^{-40}$C^{2}m^{2}J^{-1}. [b] The first-order correction to the density matrix has not converged.

and energy of MOs, net atomic charges, etc.) of $Ni(S_2C_2H_2)_2$ and $Ni(S_2C_3H_3)_2$ [bis(3-thioxopropene-1-thiolato)nickel]. They found that 3d(S) orbitals have a small effect on the ground state and the transition energies, in particular of the lower lying states. These AOs, however, appear to have a major influence in the region 30 000–50 000 cm^{-1} improving the agreement with experiment.[12f] Coffen et al. noted that: "ultraviolet spectra of tetrathioethylenes and their electrochemical properties can be rationalized by extended Hückel calculations provided that the 3d orbitals of sulfur are included in the basis set".[13] Cooper et al. in their study on TTF suggested that "inclusion of sulfur d orbitals is necessary to explain the relative lengths of the two C=C bonds".[14a]

In our previous work we have examined the effect of these orbitals on some properties of compounds which involved only sulfur bonded to carbon. Here, however, we have in addition metal–sulfur (Ni–S) bonds. In the analysis which follows, it is implicitly accepted that a basis with 3d functions for sulfur is of better quality than the one without them, because 3d(S) orbitals improve the capacity of the wave function to describe correctly molecular polarization. The practical question is whether their effect can be easily and reliably estimated, in this particular class of compounds. From the present limited set of results on NiBDT and some of its derivatives, it is observed that if, for sulfur, no d orbitals are used, we have in four cases a considerable increase in γ (**1**, 81.9%; **3**, 17.9%; **7**, 18.9%; and **8**, 24.4%).

In Table II, where the polarizability results are presented, it is seen that if the sulfur basis involves only 3s,p orbitals, the results may be larger (**1**) or smaller (**3**, **7**, and **8**) or divergence of the first-order correction to the density matrix may occur (**5**). The average difference between the polarizability sets of results (with and without d orbitals) is 10.8%. Thus, the present results indicate that for the derivatives of NiBDT, 3d(S) are essential for hyperpolarizability values. Even for the polarizability where the average difference between the two sets is not large, lack of d functions may lead to convergence problems and thus their use is recommended.

To the best of our knowledge there is no information in the literature concerning the effect of the Ni basis on the quality of the second hyperpolarizability values of organometallic molecules. Thus a large number of computational experiments were performed which eventually led to the adoption of a 3d function with exponent 3.0, because this did not create any problems in the determination of the first- and second-order correction to the density matrices[9] and it is close to the 3d exponents proposed by Karlson et al.[14b] and Li et al.[14c] (that is 2.96 and 3.06, respectively). The exponent of 4s,p (1.0) for Ni has been selected using as the criterion the optimum values for α and γ of $Ni(S_2C_2H_2)_2$, as well as the good convergence performance of $R^{(1)}$ and $R^{(2)}$.

The polarizability[6d] and hyperpolarizability[4a] values, given in Tables I and II are static. One may note, however, that the frequency dependence of these properties has been discussed by several authors.[15-17]

The criteria employed for the computation of the density matrices ($R^{(0)}$, $R^{(1)}$ and $R^{(2)}$, which are required for the calculation of the hyperpolarizability components, have been given elsewhere.[10b] The matrices $R^{(1)}$ and $R^{(2)}$ are stored in single precision, while all sums and inner products are computed in double precision.

III. Results and Discussion

We present a brief review of the relevant data for the electronic structure of NiBDT, in order to get a better insight into the factors to which the hyperpolarizability of this compound is due.[12f,18,19]

It is known that various bonding schemes are possible for this molecule. These involve 8π, 10π, and 12π electrons (in those the four nickel d_π electrons are not included), and the formal oxidation states of Ni are 0, +2, and +4, respectively.[12f] However, evidence from proton magnetic resonance spectra and infrared C–S and C–C stretching frequencies strongly suggests the adoption of the structure, which is given in Figure 1a,[12c] where the positive charge of Ni (d^8) is counterbalanced by the two negative charges in the ligands. The neutral ligand (dithioglyoxal) has 4π electrons and the dianion has 6π electrons.[20] It is added that CI computations show that the above structure accounts for 87% of the ground state description.[12f]

The nonlinearities of two fragments of NiBDT are discussed below. It is observed that γ of $S_2C_2H_2$ is only a small percentage (4.5%) of the property of $Ni(S_2C_2H_2)_2$. Addition of Ni leads to an increase in this property, but γ of $NiS_2C_2H_2$, is still a comparatively small percentage (20.5%) of the hyperpolarizability of $Ni(S_2C_2H_2)_2$. It is further noted that

$$\gamma(S_2C_2H_2) + \gamma(NiS_2C_2H_2) = 99\ 200 \text{ au}$$

while γ of $Ni(S_2C_2H_2)_2$ is 4 times larger. Similarly, for the polarizability

$$\alpha(S_2C_2H_2) + \alpha(NiS_2C_2H_2) = 194 \text{ au}$$

which is smaller than the corresponding value for $Ni(S_2C_2H_2)_2$ by a factor of 1.48.

---

(13) Coffen, D. L.; Chambers, J. Q.; Williams, D. R.; Garrett, P. E.; Canfield, N. D. *J. Am. Chem. Soc.* **1971**, *93*, 2258.

(14) (a) Cooper, W. F.; Kenny, N. C.; Edmonds, J. W.; Nagel, A.; Wudl, F.; Coopens, P. *Chem. Commun.* **1971**, 889. (b) Karlsson, G.; Zerner, M. C. *Int. J. Quantum Chem.* **1973**, *7*, 35. (c) Li, J.; Correa de Mello, P.; Jug, K. *J. Comp. Chem.* **1992**, *13*, 85.

(15) (a) Alms, G. R.; Burnham, A. K.; Flygare, W. H. *J. Chem. Phys.* **1975**, *63*, 3321. (b) Parkinson, W. A.; Zerner, M. C. *J. Chem. Phys.* **1989**, *90*, 5606.

(16) (a) Bishop, D. M.; Pipin, J. *J. Chem. Phys.* **1989**, *91*, 3549. (b) Shelton, D. P. *J. Chem. Phys.* **1986**, *84*, 404.

(17) Rosasco, G. J.; Hurst, W. S. *J. Opt. Soc. Am.* **1986**, *B3*, 1251.

(18) Schrauzer, G. N.; Mayweg, V. P. *J. Am. Chem. Soc.* **1965**, *87*, 3585.

(19) Muller-Westerhoff, U. T.; Vance, B. *Comprehensive Coordination Chemistry: The Synthesis, Reactions, Properties and Applications of Coordination Compounds*; Wilkinson, G., Ed.; Pergamon Press: Oxford, England, 1987; Vol. 2, p 595.

(20) Benedix, R.; Hennig, H. *Inorg. Chim. Acta* **1988**, *141*, 21.

The molecule is differentiated from the fragments, because in the former substantial CT and extensive delocalization of the π electrons occur. It is considered that these are two significant factors (the contribution of which in the formation of large nonlinearities is well documented[5i]) with which the large change in α/γ, on going from fragments to the molecule, should be associated.

The magnitude of the nonlinearity of NiBDT is worth commenting upon. Thus considering the molecular size and the number of electrons, this compound has a rather large γ value. For example one notes the ratio

$$\gamma[\mathrm{Ni(S_2C_2H_2)_2}]/\gamma[\mathrm{C_{10}H_8}] = 6.4$$

taking into account that $C_{10}H_8$ (naphthalene) is a 10π electron system (it is recalled that the dominant structure of $Ni(S_2C_2H_2)_2$ is also associated with 10π electrons[12c]). The corresponding ratio for the polarizability is

$$\alpha[\mathrm{Ni(S_2C_2H_2)_2}]/\alpha[\mathrm{C_{10}H_8}] = 4.3$$

For the above ratios the values for α and γ of $C_{10}H_8$ were taken from refs 21 and 22.

Greater understanding of the nonlinear polarization mechanisms and factors, which are associated with the second hyperpolarizability of NiBDT may be gained by comparing it with TTF (tetrathiafulvalene) (Figure 1b) as the structure of these compounds presents many similarities and an obvious difference: Ni is replaced by C=C. It is considered that essential for the formation of the polarization properties of TTF is the interaction of the π-type lone pair of sulfur[23a] with the π-electrons of three pairs of doubly bonded carbons. In addition the bridging C=C, which replaces Ni in NiBDT (leading to TTF), is a very polar group the effect of which increases if it can be part of a π-electron network (e.g. conjugated molecules[23b]). However, it has been observed that the α and γ values of TTF are 74.7% and 63% of the corresponding values of NiBDT. It is thus clear that Ni has a considerably more polarizable effect than C=C, in the given intramolecular environment.

One of the frequently used substituents of NiBDT is the methyl group. This is also known to have a donor ability. Thus, we have computed the nonlinearities of some methyl derivatives of NiBDT in order to discuss the effect of replacing H by CH_3 (Figure 1). Methylation of NiBDT leads to a very large increase in γ (Table I). It is also worth noting that the dimethyl derivative (**5**) has a larger γ value than the tetra- (**7**) and hexamethylated NiBDT (**8**). Comparing the properties of **5** and **7**, we have

$$\gamma_{xxxx}(\mathbf{5})/\gamma_{xxxx}(\mathbf{7}) = 116\,000/177\,000$$

$$\gamma_{yyyy}(\mathbf{5})/\gamma_{yyyy}(\mathbf{7}) = 412\,000/285\,000$$

$$\gamma_{zzzz}(\mathbf{5})/\gamma_{zzzz}(\mathbf{7}) = 2\,720\,000/698\,000$$

$$\gamma_{xxzz}(\mathbf{5})/\gamma_{xxzz}(\mathbf{7}) = 350\,000/518\,000$$

$$\gamma_{yyzz}(\mathbf{5})/\gamma_{yyzz}(\mathbf{7}) = 414\,000/383\,000$$

$$\gamma_{xxyy}(\mathbf{5})/\gamma_{xxyy}(\mathbf{7}) = 70\,500/89\,100$$

Overall, the larger γ of the dimethyl derivative, in comparison to the tetramethyl derivative is mainly due to the γ_{zzzz} component. The trend shown by the polarizabilities of methylating NiBDT is different; that is, α increases with methylation. A preliminary computation for $[Ni(S_2C_2(CH_3)_2)]^{2-}$ has shown that it has an extremely large γ value (Table I).

We have also considered the anisotropy of the hyperpolarizability, a measure of which may be given by $\gamma_{zzzz}/\gamma_{xxxx}$ ($=\gamma_1$) and $\gamma_{zzzz}/\gamma_{yyyy}$ ($=\gamma_2$), since it provides valuable information concerning the electronic structure. It is observed that NiBDT is highly anisotropic (Table I). Substitution of 2 H by methyl groups (trans, **5**) remarkably increases both γ_1 and γ_2. This is mainly due to γ_{zzzz} of **5** being much larger than that of **1**, although all three diagonal terms of **5** are larger than the corresponding ones of **1**; that is:

$$\gamma_{xxxx}(\mathbf{5})/\gamma_{xxxx}(\mathbf{1}) = 3.75$$

$$\gamma_{yyyy}(\mathbf{5})/\gamma_{yyyy}(\mathbf{1}) = 4.63$$

$$\gamma_{zzzz}(\mathbf{5})/\gamma_{zzzz}(\mathbf{1}) = 7.45$$

The tetramethyl derivative (**7**) has smaller γ_1 and γ_2 values than NiBDT. As one could have expected, further methylation of **5**, leads to a more isotropic structure in comparison to **1** or **5** (Table 1).

Finally it is observed that $\gamma_1 < 0$ for TTF. This is due to $\gamma_{xxxx} < 0$ (−39 400 au). A negative hyperpolarizability value has been termed "hypopolarizability" by Coulson et al. and has been discussed by Langhoff et al.[23c,d]

IV. Concluding Remarks

The second hyperpolarizabilities of NiBDT and some of its derivatives have been computed by employing the CHF–PT–EB–CNDO method. A point of major significance in this technique is the optimization of the basis sets. Overall it is noted that the principles which have been used to build them have been extensively tested, and it has been found that the derived functions are flexible enough so that polarization effects are adequately represented. Other important contributions (e.g. correlation effects) are taken into account, at least to some extent, through the calibration of the exponents.[7,10]

The main findings of the present work, which are expected to be useful in the design of materials for various applications (e.g. for telecommunication devices) are as follows.

a. Satisfactory treatment of the polarizability and second hyperpolarizability of NiBDT and its methylated derivatives requires the use of 3d orbitals on sulfur.

b. The large hyperpolarizability of NiBDT has been rationalized in terms of CT and delocalized π electrons.

c. TTF has smaller polarizability and second hyperpolarizability than NiBDT. This demonstrates that the overall effect of Ni is larger than that of C=C, on α and γ, in the considered intramolecular environment. This observation, together with the analysis on the fragments of NiBDT, shows the effect of the metal on the properties (α, γ) of $Ni(S_2C_2H_2)_2$.

d. The dimethyl derivative of NiBDT has a very large second hyperpolarizability, which is larger than the corresponding values for tetra- and hexamethylated $Ni(S_2C_2H_2)_2$.

e. The high anisotropy of NiBDT may be further increased by judiciously chosen substituents and the position where these will go.

The present work has demonstrated that a simple, well-optimized model (like CHF–PT–EB–CNDO) can be used to trace promising molecules for nonlinear devices as well as to rationalize the main features of their polarization properties.

Acknowledgment. The authors thank Dr. G. Papavasiliou for some useful reprints.

---

(21) Lefévre, R. J. W.; Sundaram, K. M. S. *J. Chem. Soc.* **1963**, B4442.

(22) Bethea, C. G. *J. Chem. Phys.* **1978**, *69*, 1312.

(23) (a) Tatsumi, K.; Matsubara, I.; Inoue, Y.; Nakamura, A.; Cramer, R. E.; Tagoshi, G. J.; Golen, J. A.; Gilje, J. W. *Inorg. Chem.* **1990**, *29*, 4928. (b) Hermann, J. P.; Ducuing, J. *J. Appl. Phys.* **1974**, *45*, 5100. (c) Coulson, C. A.; Maccoll, A.; Sutton, L. E. *Trans. Faraday Soc.* **1952**, *81*, 106. (d) Langhoff, P. W.; Lyons, J. D.; Hurst, R. P. *Phys. Rev.* **1966**, *148*, 18.

(24) Sartain, D.; Truter, M. *J. Chem. Soc. A* **1967**, 1264.

(25) *Tables of Interatomic Distances and Configuration in Molecules and Ions, Supplement 1956–1959*; Sutton, L. E., Ed.; Special Publication 18; The Chemical Society: London, 1965.