

Calculations of induced moments in large molecules. III. Polarizabilities and second hyperpolarizabilities of some aromatics

J. Waite, M. G. Papadopoulos, and C. A. Nicolaides

Theoretical and Physical Chemistry Institute, National Hellenic Research Foundation, Vas. Constantinou 48, Athens 501/1, Greece

(Received 5 January 1982; accepted 30 April 1982)

We report the results of calculations of the average polarizability α and second hyperpolarizability γ for benzene, naphthalene, and three different configurations of biphenyl, phenanthrene, anthracene, and pyrene. The computations were performed employing a scheme whose main elements are McWeeny's coupled Hartree-Fock perturbation theory, the CNDO approximations, and a small, properly optimized, extended basis. The mean error for the average polarizabilities is 7%. The error for the second hyperpolarizability of naphthalene is within the experimental uncertainty.

I. INTRODUCTION

A wave function sufficient for hyperpolarizabilities has to properly describe the outer regions of the molecule and the important correlation effects.¹

Rigorous treatment of these effects are computationally forbidding even for the smallest conjugated systems. So one has to adopt several approximations.

As a contribution toward the specification of a simple and yet reliable model, we have recently introduced a computational approach^{2,3} which is applied here to some aromatic systems. Their nonlinearities are of increasing interest in pure and applied research.⁴ Our model gave good results for some alkanes² and polyenes.³ Here it is shown that the polarizabilities of the studied aromatic molecules agree well with the experimental values. Thus, we hope that the hyperpolarizabilities presented here, for which no experimental measurements are available, are reliable.

II. PREVIOUS THEORETICAL WORK ON AROMATICS

We only state those theoretical approaches which have been applied to several compounds.

A. Polarizabilities

Most of the calculations on these molecules have been carried out with semiempirical methods.

Marchese and Jaffé⁵ used PT-CNDO/S-CI (for explanation of some acronyms see footnotes of Table I) for benzene, naphthalene, anthracene, and phenanthrene. The average error was 26%. Mathies and Albrecht⁶ employed FPT-CNDO/S-CI on benzene, naphthalene, and anthracene with an average error of 15%. Bounds⁷ applied FPT-INDO on benzene, naphthalene, anthracene, phenanthrene, and planar biphenyl with an average error of 53%; while for these molecules computations with PT-Hückel⁸ and VPT-PPP,⁸ carried out by Hameka's group, had an average error of 30% and 24%, respectively.

Ab initio SCF calculations with an STO-4G basis set⁹ for benzene, naphthalene, and anthracene had an average error of 45%. These results indicate that in order

for *ab initio* SCF wave functions to lead to meaningful results, polarization functions are required. Such a wave function would be extremely expensive in terms of computing time and core storage.

It should be noted that even if the Hartree-Fock limit is approached one has to consider the correlation effect, contributions from which, for this size of molecules, would exceed 10% of the total α .¹⁰ Thus, it seems that at present only refined semiempirical treatments can economically lead to meaningful results.

B. Second hyperpolarizabilities

Hameka's group has carried out extensive studies on aromatic molecules, employing VPT-CNDO/2,¹¹ PT-Hückel,¹² PT-PPP,¹² and a method which is a combination of extended Hückel and PPP.¹³ This method gave a very good γ for C₆H₆.

Hameka *et al.*¹² believe that their Hückel values are less accurate than their PPP values which they think are accurate to within a factor of 2. The problem with all theoretical models predicting γ , including our own, is the scarcity of experimental values. Consequently it is difficult to offer any reliable estimate of the model's accuracy.¹⁴

III. METHOD

The main elements of our computational scheme are^{2,3} (a) McWeeny *et al.*¹⁵ coupled Hartree-Fock perturbation theory, (b) the CNDO/2¹⁶ method extended to include an enlarged basis set and the bonding parameters proposed by Shinoda and Akutagawa,¹⁷ and (c) the optimization of the exponents of the AOs with respect to the experimental polarizability and second hyperpolarizability of a reference compound.¹⁸

The resulting basis set is then used to calculate the properties of another molecule. If this value agrees reasonably with experiment then we proceed to calculate the properties of other members of the series.³

Considerations based on atomic theory imply that high *l* functions are needed, in particular for γ .¹⁹ Thus, the set of AOs describing carbon should include *f* or -

TABLE I. Polarizabilities α (in a.u.) of some aromatic molecules.

No.	Molecule	This work	Other calculations	Method ^a	Experiment			
1	Benzene	61.86	62.06 (Ref. 5)	FPT-CNDO/S-CI	66.80 ^b (Ref. 33)			
			51.90 (Ref. 6)	FPT-CNDO/S-CI	69.51 (Ref. 34)			
			48.72 (Ref. 32)	FPT-MINDO/3				
			48.72 (Ref. 32)	FPT-MNDO				
			28.41 (Ref. 7)	FPT-INDO				
			37.07 (Ref. 8)	PT-Hückel				
			37.07 (Ref. 8)	VPT-PPP				
			53.97 (Ref. 9)	FPT- <i>ab initio</i> SCF ^e				
			58.59 (Ref. 9)	FPT- <i>ab initio</i> SCF ^f				
			32.74 (Ref. 9)	FPT- <i>ab initio</i> SCF ^g				
2	Naphthalene	115.45 ^c 114.82 ^d	121.21 (Ref. 5)	PT-CNDO/S-CI	111.8 (Ref. 35)			
			93.81 (Refs. 6 and 31)	FPT-CNDO/S-CI				
			55.00 (Ref. 7)	FPT-INDO				
			81.00 (Ref. 8)	PT-Hückel				
			87.77 (Ref. 8)	VPT-PPP				
			61.21 (Ref. 9)	FPT- <i>ab initio</i> SCF ^g				
3	Biphenyl planar Biphenyl 45° ^b Biphenyl perpendicular ^b	145.12 146.42 146.25 ^c	62.76 (Ref. 7)	FPT-INDO	152.25 (Ref. 36) 132.27 (Ref. 7)			
			4	Anthracene	183.72 ^c	225.61 (Ref. 5)	PT-CNDO/S-CI	170.97 (Ref. 33)
						159.94 (Ref. 6)	FPT-CNDO/S-CI	
89.01 (Ref. 7)	FPT-INDO							
138.23 (Ref. 8)	PT-Hückel							
157.30 (Ref. 8)	VPT-PPP							
99.25 (Ref. 9)	FPT- <i>ab initio</i> SCF ^g							
5	Phenanthrene	173.24 ^c	248.62 (Ref. 5)	PT-CNDO/S-CI	159.50 (Ref. 33)			
			81.52 (Ref. 7)	FPT-INDO				
			125.16 (Ref. 8)	PT-Hückel				
			139.68 (Ref. 8)	VPT-PPP				
			91.93 (Ref. 9)	FPT- <i>ab initio</i> SCF ^g				
6	Pyrene	205.73 ^c			190.09 (Ref. 33)			

^aPT: perturbation theory; FPT: finite perturbation theory; VPT: variation perturbation theory.

^bWith respect to this experimental result the optimization of the basis set was carried out.

^cThe experimental bond angles and lengths are those of C₆H₆ (Ref. 25).

^dThe experimental geometry is used (Ref. 26).

^eDouble-zeta basis set (Ref. 44).

^fDunning's large *sp* basis set (Ref. 37).

^gSTO-4G basis set (Ref. 38).

^hThe two rings are twisted with respect to each other by an angle of 45° (Ref. 27).

ⁱThe two rings are perpendicular (Ref. 27).

bitals. Nevertheless, the slightly extended, optimized basis set and the multicenter nature of the MOs,²⁰ apparently allows for the proper average polarization of the charge distribution—as our work on a variety of hydrocarbons indicates.^{2,3}

Every semiempirical model requires adjustment of some variable (parameters and/or orbital exponents, etc). This is not a trivial task.²¹ We believe that the calibration of the wave function by optimizing the exponents alone with respect to the experimental values of a reference molecule and the testing of this basis on another, judiciously chosen compound, allows one to maximally use the few experimental data.

It is known that the values of the hyperpolarizabilities present a severe quality test of a wave function. Even elaborate wave functions, near the Hartree-Fock limit, can fail to reproduce the experimental results.²²

On the other hand, our model is very simple, perhaps the simplest possible (the extended Hückel is considered

less satisfactory since it uses an "undefined" Hamiltonian¹¹) which includes: (a) all valence AOs; the inner shell nonbonding electrons can be assumed to contribute very little²³ and (b) the σ and π contributions simultaneously.

Thus, it is important to ask: does this simple model contain the essential characteristics of the electronic charge distortion which occurs when the molecule is placed in a uniform electric field? We think that the answer is yes because our results on alkanes,² polyenes,³ and now on the aromatics show that the calculated α and γ are in good agreement with experiment.

IV. BASIC FORMULAS

The average values of the polarizability, and the second hyperpolarizability, are given by²⁴

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

$$\gamma = \frac{1}{15}(\gamma_{xxxx} + \gamma_{yyyy} + \gamma_{zzzz} + 2\gamma_{xxyy} + 2\gamma_{xxzz} + 2\gamma_{yyzz}). \quad (2)$$

TABLE II. Second hyperpolarizabilities γ (in a. u.) of some aromatic molecules. For the acronyms see footnote to Table I.

(No.)	Molecules	This work		Other calculations	Method	Experiment
1	Benzene	24 682 ^b	24 324 ^c	73 258	VPT CNDO/2 (Ref. 11)	24 538 ± 596 ^{a,e}
				109	FPT-INDO (Ref. 39)	12 829 ± 6414 ^h
				926	PT-Hückel (Ref. 14)	18 582 ± 2779 ⁱ
				13 499	ext. Hückel-PPP ^f (Ref. 13)	
2	Naphthalene	60 313 ^{b,d} 58 404 ^{b,e}	58 266 ^{c,d}	90 292	VPT-PPP (Ref. 12)	61 942 ± 12 388 ^j
				111 674	PT-Hückel (Ref. 12)	
3	Biphenyl planar Biphenyl 45° ^k Biphenyl perpendicular ^k	72 835 ^b 75 590 ^b 73 866 ^b	80 257 ^c 81 265 ^c 81 133 ^c	118 046	VPT-PPP (Ref. 12)	
				27 993	PT-Hückel (Ref. 12)	
4	Anthracene	111 226 ^{b,d}	111 656 ^{c,d}	301 132	VPT-PPP (Ref. 12)	
				55 867	PT-Hückel (Ref. 12)	
5	Phenanthrene	101 421 ^{b,d}	102 842 ^{c,d}	221 203	VPT-PPP (Ref. 12)	
				49 077	PT-Hückel (Ref. 12)	
6	Pyrene	134 400 ^{b,d}	130 822 ^{c,d}			

^aWith respect to this experimental result, the optimization of the basis set was carried out.

^bThe CHF-PT-EB-CNDO has been used for the calculation of these results (see the text).

^cThe empirical relation $(2.8L)^{4.2}$ has been employed for the estimation of second hyperpolarizability.

^dThe experimental bond angles and lengths are those of C₆H₆ (Ref. 25).

^eThe experimental geometry is used (Ref. 26).

^fAccording to this method the π orbital contribution is given by the PPP calculation and the σ and $\sigma-\pi$ contributions by the extended Hückel.

^gdc-induced second harmonic generation, 694 nm, gas phase (Ref. 40).

^hKerr effect, 632.8 nm, gas phase. (Ref. 41)

ⁱdc-induced second harmonic generation, 1.06 μ m, liquid phase (Ref. 42).

^jdc-induced second harmonic generation, molten state (Ref. 43).

^kSee footnotes h and i of Table I.

Expressions for the components of α and γ , when the molecular wave function is approximated by a single determinant have been given by McWeeny *et al.*¹⁵

V. RESULTS AND DISCUSSION

Benzene was chosen as a reference compound and naphthalene as the test case for optimizing the basis set to be used in aromatic molecules. The optimum basis set for α is

$$\text{C: } 2s(1.625), 2p(1.625);$$

$$\text{H: } 1s(0.9), 2s(0.37), 2p(0.37),$$

and for γ is

$$\text{C: } 2s(1.325), 2p(1.325);$$

$$\text{H: } 1s(1.0), 2s(0.5), 2p(0.5).$$

The results produced by employing the above basis sets are presented in Table I for α and Table II for γ . Although in the aromatics we have used different basis for α and γ in the polyenes³ and alkanes² we have used the same basis set for both α and γ . The possibility of using different basis sets for α and γ has been noted before.³

We have calculated α and γ of naphthalene for both the symmetric (bond angles and lengths are those of C₈H₈²⁵) and the experimental geometry.²⁶ The polarizability is practically the same but γ shows a small difference for the two examined geometries. This result

indicates that γ is more sensitive than α to the geometry changes. Nevertheless, since the difference was small, we decided to use this symmetric geometry for the other molecules.

Biphenyl is known to be planar in the crystal phase. However, in solution and in the vapor phase, the two rings are twisted with respect to each other by an angle of about 45°. The twisting is the result of steric interactions.²⁷ We have calculated α and γ of biphenyl when it is planar, when the ring planes form a 45° angle and when they are perpendicular.

The polarizability and the hyperpolarizabilities have often been related, by empirical formulas, with the size of molecule.²⁸⁻³⁰

The polarizability α and the effective length L of the molecule have been related by^{28,29}

$$\alpha = L^3, \quad (3)$$

We propose that γ is related to L by

$$\gamma = (C_1 L)^{C_2}, \quad (4)$$

TABLE III. Conversion of a. u. to electrostatic and SI units.

Property	1 a. u. equals (approx.)
α	$0.148\,176 \times 10^{-24} \text{ cm}^3 \approx 0.164\,867 \times 10^{-40} \text{ C}^2 \text{ m}^2 \text{ J}^{-1}$
γ	$0.503\,717 \times 10^{-39} \text{ esu} \approx 0.623\,597 \times 10^{-64} \text{ C}^4 \text{ m}^4 \text{ J}^{-3}$

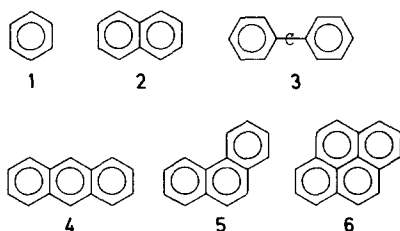


FIG. 1. Structure of the molecules that were considered.

where $C_1 = 2.8$ and $C_2 = 4.2$.

The constants C_1 and C_2 have been optimized using benzene as a reference compound and naphthalene as a test case. This empirical formula reproduces satisfactorily the calculated second hyperpolarizabilities (Table II). The largest error is for planar biphenyl (10%).

Our computations show that γ for anthracene is larger than that of phenanthrene. Similarly we have found that the *trans*-isomers of polyenes have larger α and γ than *cis*.³ This is in line with Oudar's observation according to which γ of *trans*-stilbene is larger than that of *cis*-stilbene.³⁰ This difference of γ can be understood in terms of the greater length of the *trans*-isomers and anthracene, in comparison with the *cis*-isomers and phenanthrene [Eq. (3) and Tables I and II].

CONCLUSIONS

Our proposed method for scaling the wave function has been applied to some aromatics. The mean error for the average polarizabilities is 7%. This small error could be due to the high regularity of the aromatics. As for γ , due to the lack of experimental evidence, it is difficult to substantiate any claim of accuracy. However the structural similarity of the studied compounds, and the good α results and the successful prediction of naphthalene's γ allows some optimism that the γ of the other aromatics are equally good.

¹G. D. Purvis III and R. J. Bartlett, Phys. Rev. A **23**, 1594 (1981).

²C. A. Nicolaides, M. G. Papadopoulos, and J. Waite, Theor. Chim. Acta (to be published).

³M. G. Papadopoulos, J. Waite, and C. A. Nicolaides J. Chem. Phys. **77**, 2527 (1982).

⁴H. F. Hameka, J. Chem. Phys. **67**, 2935 (1977).

⁵F. T. Marchese and H. H. Jaffé, Theor. Chim. Acta **45**, 241 (1977).

⁶R. Mathies and A. C. Albrecht, J. Chem. Phys. **60**, 2500 (1974).

⁷P. J. Bounds, Chem. Phys. Lett. **70**, 143 (1980).

⁸O. Zamani-Khamiri and H. F. Hameka, J. Chem. Phys. **71**, 1607 (1979).

⁹A. Chablo and H. Hinchliffe, Chem. Phys. Lett. **72**, 149 (1980).

¹⁰R. D. Amos and J. H. Williams, Chem. Phys. Lett. **84**, 104 (1981).

¹¹E. N. Svendsen, T. Stroyer-Hansen, and H. F. Hameka, Chem. Phys. Lett. **54**, 217 (1978).

¹²O. Zamani-Khamiri and H. F. Hameka, J. Chem. Phys. **73**, 5693 (1980).

¹³O. Zamani-Khamiri, E. F. McIntyre, and H. F. Hameka, J. Chem. Phys. **72**, 1280 (1980).

¹⁴E. F. McIntyre and H. F. Hameka, J. Chem. Phys. **69**, 4814 (1978).

¹⁵J. L. Dodds, R. McWeeny, W. T. Raynes, and J. P. Riley, Mol. Phys. **33**, 611 (1977).

¹⁶J. A. Pople and D. L. Beveridge, *Approximate Molecular Orbital Theory* (McGraw-Hill, New York, 1970).

¹⁷H. Shinoda and T. Akutagawa, Bull. Chem. Soc. Jpn. **48**, 3431 (1975).

¹⁸R. Daudel, *Quantum Theory of the Chemical Bond* (Reidel, Dordrecht, Holland, 1974).

¹⁹R. E. Sitter, Jr. and R. P. Hurst, Phys. Rev. A **5**, 5 (1972).

²⁰P. A. Christiansen and E. A. McCullough, Jr., Chem. Phys. Lett. **63**, 570 (1979).

²¹K. F. Freed, *Electronic Structure Calculation*, edited by G. E. Segal (Plenum, New York, 1977), Part A.

²²P. Lazzeretti and R. Zanasi, J. Chem. Phys. **74**, 5216 (1981).

²³D. G. Bounds and A. Hinchliffe, J. Chem. Phys. **72**, 298 (1980).

²⁴A. D. Buckingham and B. J. Orr, Q. Rev. London **21**, 195 (1967).

²⁵*Tables of Interatomic Distances and Configurations in Molecules and Ions* (The Chemical Society, London, 1965).

²⁶D. W. J. Cruickshank, Acta Crystallogr. **10**, 504 (1957).

²⁷A. Streitwieser and C. H. Heathcock, *Introduction to Organic Chemistry* (Collier-MacMillan, New York, 1976).

²⁸M. T. Khimenko, N. N. Gritsenko, and V. V. Aleksandrov, Russ. J. Phys. Chem. **49**, 1407 (1975).

²⁹A. Dulcic, C. Flytzanis, C. L. Tang, D. Répin, M. Fétizon, and Y. Hoppilliard, J. Chem. Phys. **74**, 1559 (1981).

³⁰J. L. Oudar, J. Chem. Phys. **67**, 446 (1977).

³¹H. Meyer, K. W. Schults, and A. Schweig, Chem. Phys. Lett. **31**, 187 (1975).

³²M. J. S. Dewar, Y. Yamaguchi, and S. H. Suck, Chem. Phys. Lett. **59**, 541 (1978).

³³R. J. W. LeFèvre and K. M. S. Sundaram, J. Chem. Soc. B **4442** (1963).

³⁴M. P. Bogaard, A. D. Buckingham, M. G. Corfield, D. A. Dummur, and A. H. White, Chem. Phys. Lett. **12**, 558 (1972).

³⁵R. J. W. LeFèvre and L. Radom, J. Chem. Soc. B **1295** (1967).

³⁶R. J. W. LeFèvre and D. S. N. Murphy, Aust. J. Chem. **21**, 1903 (1968).

³⁷T. H. Dunning, Jr., J. Chem. Phys. **55**, 716 (1971).

³⁸W. J. Hehre, R. Ditchfield, R. F. Stewart, and J. A. Pople, J. Chem. Phys. **51**, 2657 (1969).

³⁹J. Zyss, J. Chem. Phys. **70**, 3333 (1979).

⁴⁰J. F. Ward and D. S. Elliott, J. Chem. Phys. **69**, 5438 (1978).

⁴¹M. P. Bogaard, A. D. Buckingham, and G. L. D. Ritchie, Mol. Phys. **18**, 575 (1980).

⁴²B. F. Levine and C. G. Bethea, J. Chem. Phys. **63**, 2666 (1975).

⁴³C. G. Bethea, J. Chem. Phys. **69**, 1312 (1978).

⁴⁴L. C. Snyder and H. Basch, *Molecular Wave Functions and Properties* (Wiley, New York, 1972).