The Effect of Structural Changes on the Polarizability and Second Hyperpolarizability in Some Benzene Isomers and Their Anions

J. Waite and M. G. Papadopoulos
Theoretical and Physical Chemistry Institute, National Hellenic Research Foundation, Vas. Constantinou 48, Athens 11635, Greece

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The polarizability and second hyperpolarizability of fulvene, dimethylene-cyclobutene, trimethylene-cyclopropane, bicyclopentadiene-propane, bicyclopentadiene-propene, Dewar benzene, benzvalene and several of their anions are computed, employing a CNDO coupled Hartree-Fock procedure. The interaction of the lone pair on the anionic center with double and single bonds, the HOMO-LUMO gap, and substituent effects are employed to illuminate the structure-polarization relationship. An approximate, computationally found formula for the second hyperpolarizability is proposed.

I. Introduction

In this paper we explore the dependence of polarization on structure. This has not yet been treated extensively and systematically because of the difficulties associated with computing the hyperpolarizabilities of large molecules [1 – 3].

It is known that the ability of the charge cloud to polarize is intimately connected with the electronic and infra-red spectra, proton affinity changes, etc. [4 – 6]. In this study we concentrate on two scalar molecular parameters, the average polarizability, α and the second hyperpolarizability, γ, which respectively describe the response of molecules to small and large external electric fields. The anions of some benzene isomers and their neutral precursors have been chosen as test models. The variation of the $\widehat{\mathrm{HCC}}$ angle at the deprotonated carbon center in the anions was used as a tool to perturb the charge arrangement and to observe the induced changes in α and γ.

When classifying the collected information, two patterns of change in the electric properties emerge. These have, as distinguishing features, the association of the lone pair with (i) a double bond and (ii) single bonds. The interaction of the double bond with the lone pair was also studied as a function of their separation and the intramolecular environment. An alternative analysis of the present results comes from considering the benzene isomers as substituted ethylenes and methanes. This interpretation of the computations elucidates the extent to which substituent effects may vary the electric properties.

It has been found that the magnitude of the linearities and nonlinearities is strongly dependent on the amount of charge delocalization. It is confirmed that anions associated with extensive delocalization have, in general, nonlinearities in the same order of magnitude as their neutral precursor.

In several areas of theoretical chemistry the simple notion of electron transfer from the highest occupied MO (HOMO) to the lowest unoccupied MO (LUMO) of the same or another unit has been used to qualitatively describe complex phenomena and rationalize trends [7]. Here the energy gap between HOMO and LUMO ($=\varepsilon_{\Delta\mathrm{LH}}$), a zeroth order quantity, is employed as a qualitative probe to indicate which of two compounds is likely to be more polarizable, and moreover $\varepsilon_{\Delta\mathrm{LH}}$ is correlated to γ.

A simple computational model (CHF-PT-EB-CNDO), the reliability of which has been demonstrated, is employed for the calculations and only the properties of bound anions are reported [1 – 3].

II. Definitions and Computational Approach

A) Rigorous formulae

The average polarizability and second hyperpolarizability are given by [4]:

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$$\alpha = \tfrac{1}{3}\left(\alpha_{xx} + \alpha_{yy} + \alpha_{zz}\right), \tag{1}$$

$$\gamma = \tfrac{1}{5}\left(\gamma_{xxxx} + \gamma_{yyyy} + \gamma_{zzzz} + 2\gamma_{xxyy} + 2\gamma_{xxzz} + 2\gamma_{yyzz}\right), \tag{2}$$

where the suffices denote cartesian components.

B) *Approximate formulae*

Detailed analysis of the present results (Tables 1, 2) shows that the approximate formula

$$\gamma \cong \tfrac{1}{3}\left(\gamma_{xxxx} + \gamma_{yyyy} + \gamma_{zzzz}\right) = \gamma_{\mathrm{d}} \tag{3}$$

describes reasonably well the average second hyperpolarizability. Examination of the 29 neutral molecules and anions presented here demonstrates that γ estimated by (3) has an average error of 8% in comparison to γ calculated by the rigorous formula (2). It should be noted that (3) has already been tested on more than 100 molecules in order to verify its applicability [8]. The results were remarkably good having an average error of 8%. Use of the approximate formula (3) halves the computational cost required for the determination of γ.

The range of the applicability of (3) does not cover molecules in which the diagonal terms differ in sign. In such a case the present results show that γ can be approximated by

$$\gamma \cong \tfrac{1}{2}\left(\gamma_{xxyy} + \gamma_{xxzz} + \gamma_{yyzz}\right) = \gamma_c\,. \tag{4}$$

The average error for the relevant results of the trimethylene-cyclopropane (TMCP) anions is 7% (Table 1). However, this formula has been less extensively tested in other classes of compounds due to scarcity of molecules with the above defined restriction.

C) *Computational method*

Our computational method (CHF-PT-EB-CNDO) has been presented elsewhere in detail [1–3]. We briefly state here that it employes a CNDO wave function [9] defined in terms of an extended, properly optimized basis set. The wave function is perturbed by employing the theory developed by McWeeny and his coworkers [10].

The adequacy of CHF-PT-EB-CNDO for this study is supported by the following facts [1–3, 11]:

(a) The computational method takes into account to a considerable extent correlation effects important for the calculation of α and particularly γ via optimization of the basis sets with respect to the experimental properties.

Table 1. Polarizabilities and hyperpolarizabilities of fulvene, TMCP, DMCB and some of their anions in a.u. (Conversion factors to e.s.u. and SI are given in Table 7).

Molecule[a]	α	γ	γ_{d}[e]	Error [%]	γ_{c}[k]	Error [%]
Fulvene, 1	95	59 500	63 000	5.9		
2[b]	115	134 000	134 000	0.0		
3[b]	128	308 000	362 000	17.5		
4[b]	118	205 000	233 000	13.6		
4[c]	146	414 000	425 000	2.6		
4[d]	170	557 000	475 000	14.7		
TMCP, 5	104	48 100	53 000	10.2		
6[b, f]	173	222 000			221 000	0.4
6[g, h]	173	240 000			221 000	7.9
7[h]	216	339 000			382 000	12.7
DMCB, 8	97	64 800	72 100	11.3		
9[b]	117	241 000	257 000	6.6		
10[b]	120	254 000	290 000	14.2		
11[b]	126	285 000	309 000	8.4		
11[i]	149	509 000	556 000	9.2		
11[j]	175	740 000	742 000	0.3		

[a] The structure of fulvene, TMCP, DMCB and their anions are presented in Figure 1. The geometries are from [15].

[b] Deprotonation leaves all other bond lengths and angles unchanged.

[c] The bond $C_6{-}H_{12}$ is rotated into the molecular plane by $\varphi = 29.3°$ compared to [b]. This value is one quarter of the $\widehat{HCH}$ angle in Fulvene 1.

[d] The bond $C_6{-}H_{12}$ is colinear with the bond $C_5{-}C_6$.

[e] Equation (3) defines this symbol.

[f] γ_{xxxx} is negative. The z-axis is the dipole moment direction.

[g] The bond $C_4{-}H_8$ is colinear with the bond $C_3{-}C_4$.

[h] γ_{yyyy} is negative.

[i] The bond $C_5{-}H_{10}$ is rotated into the molecular plane by 29.3°. See footnote c.

[j] The bond $C_5{-}H_{10}$ is colinear with the bond $C_4{-}H_5$.

[k] Equation (4) defines this symbol.

(b) It employes polarization and diffuse functions which are essential for the correct description of these properties.

Further, the employment of a single method (and basis set) allows for internal consistency of the described general trends and features.

The following basis set has been used:

C: 2s(1.325), 2p(1.325),

H: 1s(0.8), 2s(0.4), 2p(0.4).

This basis has been shown to satisfactorily describe α and γ of a large number of polyenes [2] and was used here for all atoms, including those in an aliphatic environment, for comparability.

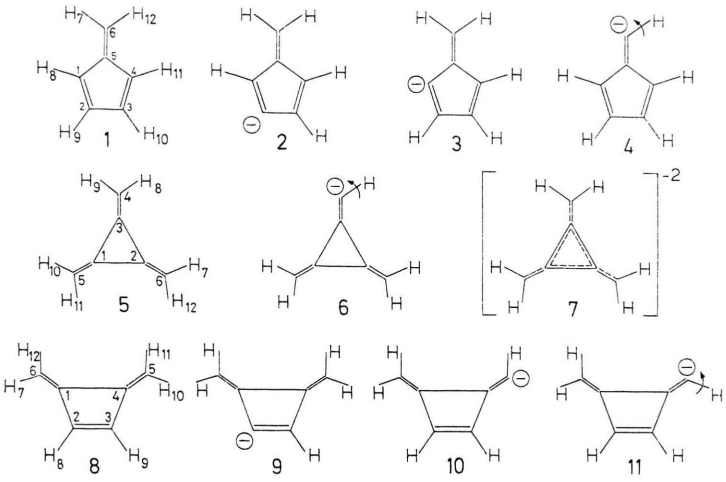

Fig. 1. Structure of fulvene, TMCP, DMCB, and some of their anions.

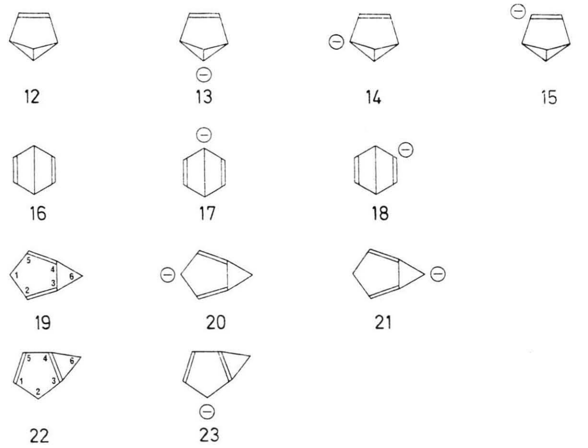

Fig. 2. Structure of BV, DB, PP1, PP2 and some of their anions.

III. Classification of Benzene Isomers

The benzene isomers are described by the empirical formula C_6H_6 and can be separated into two groups [12].

(a) Methylene isomers

The distinguishing feature of this class of isomers is that they do not have six unique C−H bonds. To this series belong 211 compounds most of which are unknown. Examples of this group of isomers are: fulvene, dimethylene-cyclobutene (DMCB), trimethylene-cyclopropane (TMCP), bicyclopentadiene-propane (PP1) and bicyclopentadiene-propene (PP2) [12].

(b) Valence isomers

This family can be described by the formula $(CH)_6$. Examples are: Dewar benzene (DB) and benzvalene (BV).

IV. Results and Discussion

The benzene isomers have been the subject of considerable theoretical and experimental research [13]. In the analysis which follows, first we consider fulvene, dimethylene-cyclobutene (DMCB), trimethylene-cyclopropane (TMCP) and some of their singly charged anions (Fig. 1) and second benzvalene (BV), Dewar benzene (DB), bicyclopentadiene-propane (PP1), bicyclopentadiene-propene (PP2) and several of their anions (Figure 2). In both groups of anions the movement of the proton attached to the negative site was also studied. For the first group of anions the variation of the hydrogen's position was in the molecular plane, while in the second series this bond moves in a plane perpendicular to the CCC plane (where the central carbon is that from which a proton has been removed).

A) Fulvene, dimethylene-cyclobutene (DMCB), trimethylene-cyclopropene (TMCP)

After deprotonation of a methylene group in fulvene or DMCB it is found that the linear and nonlinear polarizabilities of the resultant anions are very sensitive to rotation of the remaining hydrogen by an angle φ (Fig. 1) in the molecular plane

(Table 1). While deprotonation of a methylene group in TMCP and similar rotation of the remaining hydrogen showed that α and γ of TMCP were relatively insensitive to such a change. Consideration of the atomic charges, as estimated by EB-CNDO, shows that only 0.2 of an electron remains on the deprotonated carbon of TMCP while 0.7 e stay on the respective carbons of fulvene and DMCB. Past experience indicates that the large changes in α and γ with φ, observed in the negative ions of fulvene and DMCB, can be partially attributed to this large concentration of charge.

It is considered that the interaction of the lone pair on the carbon anionic center, formed by deprotonation, with the neighbouring double bond is of primary importance in the understanding of the computed results. As the rotated $^{-}$CH bond tends to colinearize with the double bond, the overlap of the latter with the lone pair increases. The results show that the variation of the interaction of the lone pair with the electron system follows the same trend as the electric properties. This observation may be rationalized by considering that the increasing penetration overlap of the double bond by the lone pair is associated with increasing bielectronic repulsions and thus higher polarization.

It is known that there is a relationship between the extent of molecular polarization and molecular excitation. Another aspect of this association is the connection between the electric properties and the inverse of $\varepsilon_{\Delta \mathrm{LH}}$. Its change in general follows the same trend (Table 2). This can be of practical use since, if the $\varepsilon_{\Delta \mathrm{LH}}$ of two compounds are known, one may qualitatively predict which is likely to be more polarizable.

Table 2. The $\varepsilon^{a}_{\Delta \mathrm{LH}}$ (in a.u.) of some considered anions.

Anion[b]		$\varepsilon_{\Delta \mathrm{LH}}$
Fulvenyl,	4^{b}	0.250
	4^{c}	0.219
	4^{d}	0.206
TMCP^{-},	6^{b}	0.201
	6^{g}	0.228
DMCB^{-},	11^{b}	0.227
	11^{i}	0.197
	11^{j}	0.187
PP1^{-},	20^{b}	0.122
	20^{c}	0.132
	21^{b}	0.223
	21^{c}	0.227
	21^{d}	0.229
PP2^{-},	23^{b}	0.287
	23^{c}	0.289

[a] $\varepsilon_{\Delta \mathrm{LH}} = \varepsilon_{\mathrm{LUMO}} - \varepsilon_{\mathrm{HOMO}}$.

[b] The superscripts of molecules numbered 4, 6 and 11 refer to footnotes of Table 1 while those of 11, 20, 21 and 23 refer to footnotes of Table 3.

It is also to be noted that the electric properties, and in particular the hyperpolarizabilities, reflect the changes in molecular structure much more sensitively than the energy (e.g. the electronic energy of 4^{d} differs from that of 4^{b} by 0.3% while the second hyperpolarizability by a factor of 3). Thus the electric properties not only give information which is complementary to that given by the energy (in the sense that the energy mainly probes the inner parts of the charge cloud while the electric properties the outer regions) but further they may disclose refined details and differences of the changing molecular structure.

B) Dewar-benzene (DB) and benzvalene (BV)

The results from BV and DB allow a further illumination of the interaction of the double bond with the lone pair. The parameters which are considered include the distance between them and the different molecular environment at the anionic center.

It is observed that the effect of this interaction is inversely proportional to the distance between the double bond and lone pair. Comparison of the results for the pairs 14, 15 and 17, 18 (Table 3) disclose the important role of the intramolecular environment in the formation of the magnitude of this contribution. The larger electric properties of 18 in comparison to those of 15 are rationalized by considering that in the former the lone pair interacts with two double bond while in the latter with only one.

C) Bicyclopentadiene-propane (PP1) and bicyclopentadiene-propene (PP2)

It is noted that PP1 deprotonated at C_6 (Fig. 2) leads to higher linearities and nonlinearities than when it is deprotonated at C_1. This may be interpreted by considering that the bond lengths C_6-C_5 and C_6-C_4 are shorter than the bond lengths C_1-C_2 and C_1-C_3. Thus there is an increased interaction between the double bond and the negative charge. Further, the greater strain with which C_6 is associated with which C_6 is associated in comparison to C_1 may be partly responsible for the higher α and γ values of 21 (Fig. 2) in comparison with those of 20.

Table 3. Polarizabilities and hyperpolarizabilities of Benzvalene, Dewar benzene, PP1, PP2 and some of their anions in a.u.

Molecule[a]	α	γ	γ_d^e	Error [%]
Benzvalene, 12	90	75 700	76 000	0.4
13	116	232 000	199 000	14.2
14	124	296 000	329 000	11.1
15	128	365 000	408 000	11.8
Dewar benzene, 16	87	71 700	59 800	16.6
17	108	152 000	138 000	9.2
18	136	582 000	549 000	5.7
PP1, 19	98	103 000	115 000	11.6
20[b]	113	177 000	178 000	0.6
20[c]	111	174 000	178 000	2.3
21[b]	131	302 000	306 000	0.3
21[c]	128	258 000	261 000	1.2
21[d]	127	243 000	245 000	0.8
PP2, 22	99	89 500	83 000	7.3
23[b]	110	160 000	139 000	13.1
23[c]	107	148 000	130 000	12.2

[a] The structure of the molecules is presented in Figure 2. The geometries are from [15].

[b] Deprotonation leaves all other bond lengths and angles unchanged.

[c] The H$-$C$^-$ bond forms an angle $\varphi = 29.3°$ with the molecular plane. This value is one quarter of the H$\hat{C}$H angle in 19.

[d] The H$-$C$^-$ bond lies on the molecular plane.

[e] Equation (3) defines this symbol.

Table 4. Variation of α and γ (in a.u.) of $C_2H_3^{-1}$ with the angle Θ (Figure 3).

Angle, Θ	α	γ
90°	32.6	11 100
74.35°[a]	33.4	12 000
58.7°[b]	36.6	15 200
30.0°	43.4	32 000
10.0°	48.3	47 000
2.0°	49.1	49 300
0.0°	49.2	49 400

[a] 74.35 = (90 + 58.7)/2.

[b] Expt. [2].

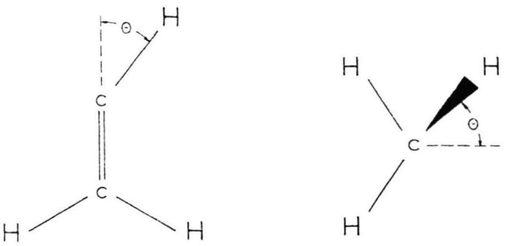

Fig. 3. Structure of $C_2H_3^{-1}$ and CH_3^{-1}.

The present calculations show that:

(a) PP1 deprotonated at C_1 is accompanied by an increase in the charge of this carbon equal to 0.12 electron, e, while

$$\gamma^-/\gamma^0 \cong 1.7\,,$$

where γ^- and γ^0 are the hyperpolarizabilities of the anion and neutral compound, respectively. The geometry of the anion is the same as that of the neutral compound.

(b) PP1 deprotonated at C_6 leads to an increase of charge equal to 0.3 e on the deprotonated carbon, while

$$\gamma^-/\gamma^0 \cong 2.9\,.$$

(c) PP2 deprotonated at C_1 is associated with an increase of the charge on that carbon equal to 0.18 e; and

$$\gamma^-/\gamma^0 \cong 1.8\,.$$

These results provide further evidence that the concentration of charge at the deprotonated carbon is one of the main parameters which affect the magnitude of the molecular electric linearity and nonlinearities.

An essential point concerning PP1 and PP2 compared to fulvene, dimethylene-cyclobutene (DMCB) and trimethylene-cyclopropane (TMCP) is that the former have an sp^3 carbon deprotonated, while the latter an sp^2. The computations on PP1 and PP2 show that, as φ (the angle of $^-$CH with the molecular plane) decreases so do the electric properties (presumably due to increased delocalization of charge on tending to planarity).

It is also noted that in the majority of cases $\varepsilon_{\Delta LH}^{-1}$ predicts the trend of this change. This observation indicates the prominence of the energy gap between the ground and the first excited state in the understanding of molecular polarization.

D) Doubly charged anion of trimethylene-cyclopropane (TMCP^{-2})

Computations on TMCP^{-2} have also been performed. This dianion was found, by EB-CNDO, to be bound; while the dianions of fulvene, DMCB etc. were unbound. It is considered that the extensive delocalization which is allowed by the TMCP structure is instrumental in the stabilization of this dianion [11a]. Further evidence for this view has been

Table 5. Variation of α and γ (in a.u.) of CH_3^{-1} with the angle[a] Θ.

Angle, Θ	α	γ
55°	24.4	5700
36	25.1	5660
18	25.4	5600
planar	25.5	5590

[a] The angle is defined by the molecular plane (HCH) and the other CH bond, whose projection bisects the $H\hat{C}H$ which defines the molecular plane. The $H\hat{C}H$ angle is 108° and corresponds to the $C\hat{C}C$ angle in a regular five membered ring.

Table 6. Variation of α and γ (in a.u.) of CH_3^{-1} with the angle[a].

Angle	α	γ
55°	25.0	5660
36°	25.7	5520
18°	26.0	5440
planar	26.1	5400

[a] The angle is defined by the molecular plane (HCH) and the other CH bond, whose projection bisects the $H\hat{C}H$ which defines the molecular plane. The $H\hat{C}H$ angle is 60° and corresponds to the $C\hat{C}C$ angle in a regular three membered ring.

Table 7. Conversion of a. u. to electrostatic and SI units.

Property	1 a. u. equals (approx.)
α	0.148176×10^{-24} esu $\cong 0.164867 \times 10^{-40}$ $C^2\,m^2 J^{-1}$
γ	0.503717×10^{-39} esu $\cong 0.623597 \times 10^{-64}$ $C^4\,m^4 J^{-3}$

found in computations in other dianions, such as $C_8H_8^{-2}$, $C_8H_6^{-2}$ [11 a].

It is also noted that $TMCP^{-2}$ and the above mentioned dianions have polarizabilities and hyperpolarizabilities within the same order of magnitude as their uncharged precursors, contrary to that which is observed in atomic negative ions [14].

E) Substituent effects

To confirm the effect of hydrogen rotation at the deprotonated carbon centers, computations of electric property variations in the model compounds $C_2H_3^{-1}$ and CH_3^{-1} were performed (Figure 3). The results of $C_2H_3^{-1}$ (Table 4) show that, as the penetration of the double bond by the lone pair increases so do the properties of interest. This trend is in agreement with that observed in fulvene and dimethylene-cyclobutene (DMCB). However, considering the benzene isomers as substituted ethylenes (fulvene, dimethylene-cyclobutene, trimethylene-cyclopropane, Dewar benzene, and benzvalene) and as substituted methanes (bicyclopentadiene-propane and bicyclopentadiene-propene), the effect of the intramolecular environment, and the substituents, specifically, becomes clear. Taking fulvene as an example we see that the hyperpolarizability of 1 and 4[d] differ (approx.) by 5×10^5 a.u., while in the case of ethylene the corresponding difference is (approx.) 4×10^4 a.u. It is thus observed that the substituent effect may substantially affect the double bond/lone pair contribution (Tables 1 and 4).

The substituent effect is also illustrated by comparing the results of $PP1^{-1}$ and $PP2^{-1}$ with those of CH_3^{-1} (Tables 5 and 6). It is seen that γ of CH_3^{-1}, on rotation of the ^{-}CH towards the molecular plane, follows the trend observed in $PP1^{-1}$ and $PP2^{-1}$. Changes in the polarizability of CH_3^{-1} induced by rotating this bond are negligible.

V. Conclusions

The benzene isomers provide a rich isoelectronic environment for the investigation of the structure-polarization relationship. The methodology followed was essentially comparative using a simple computational model whose realiability has been confirmed, and thus any absolute errors in the property values are not likely to change the main conclusions.

The question of how isomerism affects α and γ of some negative ions and their neutral precursor has been treated in a systematic way.

The hyperpolarizability is established as a powerful probe which follows, with sensitivity, changes induced in the charge cloud by variations of the intramolecular environment of anions. Thus γ is shown to be a unique tool in the study of substituent effects and intramolecular interactions in negatively charged species.

It is noted that the information given by γ is complementary to that obtained from energy calculations and thus the hyperpolarizability is an essential element in the formation of a comprehensive picture of the charge cloud.

The contribution to the properties of an interacting double bond with a lone pair is inversely proportional to their separation and very sensitive to the intramolecular environment.

It has been confirmed that the doubly charged anion, in which extensive delocalization occurs, is associated, in general, with a relatively low hyperpolarizability (within the same order of magnitude as its uncharged precursor).

The diffuse charge cloud obtained by the formal addition of electrons has some similarities to the distribution resulting from excitation. Thus it is not surprising that $\varepsilon_{\Delta \mathrm{LH}}$, a parameter employed to rationalize excitation phenomena, has been shown to be of use in the description of polarization. It has been shown that in the majority of cases, $\varepsilon_{\Delta \mathrm{LH}}$ predicts the variational trend in α and γ with changing $\widehat{\mathrm{HCC}}$ angle. The concentration of charge at the deprotonated carbon has also been used as a qualitative index to follow the changes in the polarization constants.

Further we have proposed and tested a simple, computationally found, formula for the easy determination of the molecular second hyperpolarizability.

In summary the reported results and associated analysis demonstrate and interpret the effect of structural changes (which may be due to geometric or molecular charge variations) on two important electric properties (α and γ) employing a carefully tested theoretical method (CHF−PT−EB−CNDO).

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