Electric dipole polarizability and hyperpolarizability of NCCN, NCCP, and PCCP

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Abstract. Components of the static electric dipole polarizability (α), and second hyperpolarizability (γ) tensors have been determined by accurate ab initio calculations for three molecules containing two conjugated carbon – nitrogen and/or carbon – phosphorus triple bonds. For the NCCP molecule the dipole moment (µ) and non-vanishing components of the first hyperpolarizability (β) tensor have also been calculated. Electron correlation effects have been taken into account by the second-order Many Body Perturbation Theory (MBPT(2)), and coupled cluster (CCSD and CCSD(T)) calculations. The basis set developed by Sadlej (Pol) and designed to be used in electric properties calculations together with its extension (HyPol) have been applied and compared to the results obtained with the standard aug-cc-PVTZ sets of Dunning.

Keywords: Electric dipole polarizability, hyperpolarizability, electron correlation, π-conjugated molecules

Mathematics Subject Classification: 81V55

1. Introduction

Electric response properties of atoms and molecules are known to account for a variety of their physico-chemical features and are underlying the molecular interpretation of different phenomena like refraction, absorption and scattering of electromagnetic radiation, intermolecular interactions [1,2], to mention just a few best known examples. To define the so – called dipole properties one usually expands the field dependent (induced) dipole moment µ_i(F_j) or the perturbed total energy E(F_j) into a Taylor series with respect to the electric field strength. The electric dipole polarizability tensor (α_ij), characterizes linear dependence of the induced dipole moment (µ_i) on the applied external electric field F_j, (i, j = x, y, z). The leading higher-order terms are referred to as the first (β_ijk) and second hyperpolarizabilities (γ_ijkl), respectively [2]. Because of their relevance for nonlinear optical (NLO) phenomena [3,4] these higher-order terms are objectives of particularly intense experimental and theoretical interest.

In the NLO-related applications one looks for materials with a very strong nonlinear response to the external electromagnetic field. At the molecular level this leads to the search for molecules with large values of the hyperpolarizabilities β and γ [4–6]. Among molecules of potential use in NLO-related applications, the organic molecules with spatially extended, conjugated π-bonds are of particular

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interest [8]. Accurate calculations of $\beta$ and $\gamma$ can provide useful data which are often difficult to obtain experimentally.

Recently, Miadoková, Kelló and Diercksen (MKD) [7] have estimated components of the $\alpha$ and $\gamma$ tensors for a group of linear dicyanopolyacetylenes, NC − (CC)$_n$ − CN, $n = 0, 1, 2, 3$. For the whole set of the investigated molecules they used moderately sized basis sets derived from the original Pol sets developed by Sadlej [9,10] and the second-order many-body perturbation theory (MBPT(2)) often referred to as MP2, Møller-Plesset (MP2). The first member of the series was additionally investigated by using the CCSD and CCSD(T) levels of approximations. The calculated value of the parallel component of the second hyperpolarizability $\gamma_{zzzz}$ along the chain with three conjugated triple carbon–carbon bond, i.e. $n = 3$, has been found to be impressively large, exceeding the value of $1.5 \cdot 10^6$ a.u., or in the SI units $9.3 \cdot 10^{-59}$ ($C^4m^4J^{-3}$).

Systematic computational study of (hyper)polarizabilities of well–selected groups of molecules with conjugated $\pi$-bonds and different heteroatoms undoubtedly contributes to our knowledge and understanding of potentially useful NLO-relevant systems at the molecular level. The choice of systems for the present study (NCCN, NCCP, and PCCP) is motivated by some unusual features of their electronic structure. The first of them has already been investigated by Miadoková et al. [7] and is included here because of some differences in computational details and the comparative character of the present study.

In molecules with triple bonds the electron correlation contribution to the dipole polarizability $\alpha$ has been shown to be very small and negative, i.e., correlated values for both components are slightly smaller than the respective SCF values [11,12]. The same pattern can be observed for conjugated dienes [13]. The presence of the CN group modifies this pattern. However, the overall correlation contribution to the dipole polarizability remains very small. For the series of XCN ($X = \text{halogen atom}$) molecules the electron correlation contribution to the rotational average of the dipole polarizability, $\alpha_{av}$, as estimated at the MP2 level of approximation, amounts to less than 3 per cent [14]. Similar conclusions can be drawn from the results for small cyano-substituted organic molecules [11] and linear dicyanopolyacetylenes [7]. This observation could be of great practical significance for it means that uncorrelated, low-cost SCF calculations could yield reasonably accurate results for the polarizability tensor $\alpha$. The main factor affecting the accuracy of the calculated data is then the basis set choice. This finding and attractive consequences which may follow are much in contrast with conclusions obtained for other systems. Usually a significant amount of the electron correlation must be taken into account in order to obtain reasonable values of the (hyper)polarizability tensor [6]. Therefore, it would be of important practical consequences to find out whether the chemically related CP group displays the same pattern of the negligible electron correlation contribution to the dipole polarizability $\alpha$. One should mention, however, that the correlation corrections for the second hyperpolarizability tensor $\gamma$ do not seem to follow this pattern, and their contribution to $\gamma$ of the NCCN molecule has been found to be significant [7].

The two main problems which arise in calculations of (hyper)polarizabilities are the choice of the basis set to describe properly the molecular wavefunction in the presence of an external electric field and taking into account electron correlation effects. Let us briefly address the latter problem first. We have employed advanced but standard and well-documented quantum chemical methods, namely the coupled cluster (CC) method including single and double excitations (CCSD) [22] and the improved CC scheme in which triple excitations are treated approximately (CCSD(T)) [23]. In the coupled cluster method the dynamical electron correlation is introduced in a very efficient way through infinite partial summation of important terms originating in the many-body perturbation theory. The CCSD – based methods have been proved to give excellent results for molecular properties [24,25]. The MBPT(2) results, which are obtained as a by – product in the process of the iterative solution of the CC equations can be regarded as
a valuable alternative to those of the CC methods, especially for larger systems. Usually the MBPT(2) results are acceptably accurate while the corresponding calculations are much less demanding [6,22].

The choice of the basis set appears to be the most important factor in achieving high accuracy in electric properties calculations. In this respect the approach pursued by Maroulis and his coworkers [12–14] is oriented towards obtaining the most accurate data for small systems and consists of a careful, step-by-step extension and optimization of some thoughtfully selected parent sets of functions. The resulting basis sets are large, designed for particular systems and when employed with advanced ab initio methods may yield state-of-the-art results for many small molecules. This approach for obvious reasons cannot be applied for larger systems. We have adopted a different approach here by using two much smaller sets: Pol [9,10] and their extension HyPol [26] designed for hyperpolarizability calculations. Sadlej [9] used the so-called basis set polarization method to develop small-sized basis sets designed especially for electric properties calculations. Contraction coefficients of the Pol set are determined by modelling the behavior of a single Gaussian-type orbital in the external electric field [27–29]. The Pol basis sets have been shown to yield accurate results not only for the dipole polarizability $\alpha$ but also for properties like Raman intensities (geometric derivatives of the polarizability tensor) [30], and recently polarizabilities calculated by the B3LYP density functional method, e.g. [31]. The recent review of Pol basis sets and their generation can be found in Ref. [32].

For the purpose of calculations of molecular hyperpolarizabilities the original Pol sets have been augmented with the second-polarization shell (f orbitals for C,N) and made additionally more diffuse. This extension is known as the HyPol sets [26] and has been successfully used in several applications [33–36]. The size of the HyPol basis [5s3p3d2f] for the N,C atoms and [7s5p3d2f] for phosphorus is not particularly large and makes the HyPol sets applicable to larger systems.

To study the above-mentioned aspects of the interplay between the electronic structure and electric properties, and the possible NLO-oriented applications, we have chosen three molecules with a pair of conjugated triple bonds: NCCN cyanogen (1,4-diazabutadiyne), and its phosphorus analogues NCCP (1,4-azaphosphabutadiyne or C-cyanophosphaethyne), and PCCP (formally called 1,4-diphosphabutadiyne). Cyanogen has been a subject of many detailed theoretical studies [11,15,16]. Its optimized geometry obtained at the CCSD(T) level with an extended basis set has been determined and it agrees very well with experimental data [15]. Ding et al. [17] have recently analyzed the potential energy surfaces of many possible isomers of $C_2NP$, while Pham-Tran et al. [18] analyzed potential energy surfaces of the $C_2NP$ isomers at the CCSD(T) and B3LYP levels of approximation. Both groups have found that the linear NCCP structure is by far the global energy minimum. The PCCP geometry has been determined by Jones et al. [19] using the quadratic Configuration Interaction method with single- and double- excitations and the augmented 6-311G basis set (QCISD/6-311G(2d)), and by the Bickelhauts [20] in their detailed density functional analysis of the stability of the $C_2P_2$ isomers. Both investigations point to the symmetric, linear structure of PCCP as the global energy minimum.

The electric properties of the three molecules, except for NCCN, are less known. The dipole polarizability of NCCN has been calculated by Kobayashi et al. [16] using the coupled cluster approach with a variety of basis sets. Fowler and Diercksen have carried out the fourth-order MBPT calculations [11]. The most recent results are those obtained by Miadoková et al. in the CCSD(T) approximation with amended Pol – type basis sets. Bizzocchi et al. [21] calculated the dipole moment of NCCP at the CCSD(T)/cc-pVQZ level of approximations. To the best of our knowledge no data for polarizability and hyperpolarizabilities of NCCP and PCCP seem to be available.
2. Computational methods

The total energy of a molecule perturbed by the external static homogenous electric field $F_i$ can be expressed as:

$$E = E^0 - \mu_i F_i - \frac{1}{2} \alpha_{ij} F_i F_j - \frac{1}{6} \beta_{ijk} F_i F_j F_k - \frac{1}{24} \gamma_{ijkl} F_i F_j F_k F_l - \ldots$$  \hspace{1cm} (1)

where $F_i$ denotes the external field strength along the $i$-th direction, $\mu$, $\alpha$, $\beta$, and $\gamma$, with appropriate cartesian coordinate labels as subscripts, denote the dipole moment, dipole polarizability, and first and second hyperpolarizability tensors, respectively. Eq. (1) is simpler than the general expression given by Buckingham [2] owing to the neglect of higher multipole moments and the assumed homogeneity of the perturbing electric field. The summation over repeated indices is implied.

Only the static, i.e., frequency independent electric (hyper)polarizabilities are considered in this paper. Their calculations are carried out at the SCF, MBPT(2), CCSD and CCSD(T) levels of approximation [41, 22]. The electron correlation contribution to (hyper)polarizabilities is calculated for valence electrons only.

The results presented in this paper have been obtained by using both analytical and numerical methods. At the SCF level $\alpha$ and $\beta$ tensors have been calculated analytically employing Gaussian 98 [37] program. The second hyperpolarizability $\gamma$ i.e., the fourth derivative of the total perturbed energy has been obtained in a mixed numerical-analytical procedure. In the first step the field dependent polarizability tensor $\alpha_{ii}(F_j)$ has been obtained analytically for selected values of $F$ ranging from 0.0010 to 0.0025 a.u. Then, $\alpha_{ii}(F_j)$ has been differentiated twice to yield $\gamma_{iijj}$. The first derivative represents the off – diagonal component $iij$ of the first hyperpolarizability tensor $\beta$ and has been used to obtain its $xxz$ component for the NCCP molecule.

The same two – step procedure has been applied to calculate all components of the $\gamma$ (and $\beta$ for NCCP) tensor at the MP2 level where the analytical routine to determine second-order derivatives is available in the Gaussian 98 package. All properties at the CCSD and CCSD(T) levels of theory have been calculated numerically using the values of the external field strengths listed above. The numerical accuracy of both numerical and mixed analytical-numerical schemes is sufficiently high to make meaningful all decimals of the data reported in this paper. The spherical Gaussian functions are used in all cases.

We used the Gaussian 98 suite of programs [37] for all SCF and MP2 results reported here. The CC data have been obtained using the AcesII package [38]. In the course of the CC calculations MBPT(2) and SCF results are obtained and the numerical finite – field procedure is used to yield electric response properties. The differences between numerical values obtained by AcesII and analytical (or mixed analytical-numerical) results of Gaussian 98 are within the precision of the reported data.

We have employed the newest generation of the Pol basis sets [26,32] which differs from the early Pol basis sets [9,10] by the use of general contractions in the core region. One should mention, however, that the electric properties calculated with either of the two sets are only marginally different. The HyPol sets are those described earlier [26]. The details of the Pol and HyPol basis can be obtained directly from the author or from the web page [39].

At the SCF and MP2 levels we have also performed comparative calculations using one of the correlation-consistent basis sets of Dunning [40], the aug-cc-pVTZ set. For the C and N atoms this set consists of [5s4p3d2f] contracted functions and is slightly larger than our HyPol set ([5s3p3d2f]). The good performance of the aug-cc-pVTZZ ($X = T, Q, \ldots$) basis sets in the dipole polarizability calculations has been reported [40] and it is of interest to study their efficiency in calculations of hyperpolarizabilities.
Table 1
Dipole properties of the NCCN molecule\textsuperscript{a).} Calculations with Pol and HyPol basis sets and their comparison with the aug-cc-PVTZ results. All values in a.u

|       | $\alpha_{zz}$ | $\alpha_{xx}$ | $\alpha_{zzz}$ | $\alpha_{xxxx}$ | $\alpha_{xzz}$ |
|-------|---------------|---------------|----------------|----------------|----------------|
| SCF   | 53.66         | 21.39         | 6.5            | 2.4            | 1.2            |
| Pol   | 53.68         | 21.79         | 6.0            | 2.2            | 1.0            |
| HyPol | 53.80         | 21.74         | 5.9            | 1.7            | 0.9            |
| aug-cc-PVTZ | 53.80 | 21.79 | 5.9 | 1.7 | 0.9 |
| MBPT(2) | Pol    | 52.14         | 21.49         | 9.7            | 2.5            | 1.4            |
| HyPol | 52.10         | 22.02         | 9.2            | 2.4            | 1.3            |
| aug–cc–PVTZ | 51.94 | 21.79 | 8.8 | 1.7 | 1.1 |
| MKD \textsuperscript{c)} | 54.11 | 21.72 | 10.36 | 2.63 | 1.45 |
| CCSD  | Pol           | 52.18         | 21.46         | 8.8            | 2.5            | 1.3            |
| HyPol | 52.16         | 21.96         | 8.2            | 2.3            | 1.2            |
| MKD \textsuperscript{c)} | 54.25 | 21.73 | 9.38 | 2.58 | 1.37 |
| CCSD(T)| Pol         | 53.49         | 21.73         | 9.7            | 2.6            | 1.4            |
| HyPol | 53.43         | 22.25         | 9.0            | 2.5            | 1.3            |
| MKD \textsuperscript{c)} | 55.68 | 22.00 | 10.26 | 2.76 | 1.47 |

\textsuperscript{a)} The molecule lies on the $z$ axis of the coordinate system. Experimental geometry data taken from [15].

\textsuperscript{b)} The listed results should be multiplied by $10^3$.

\textsuperscript{c)} The work of Miadoková, Kellò, and Diercksen (MKD) [7]. The basis used is the standard, segmented Pol basis set.

3. Results and discussion

3.1. Electric properties of NCCN

The polarizability $\alpha$ and second hyperpolarizability $\gamma$ tensors for the NCCN molecule are presented in Table 1. The experimental geometry used in our calculations was taken from the work of Botschwina and coworkers [21]. The values of the dipole polarizability can be compared to the results of Kobayashi et al. [16], Fowler and Diercksen [11], and the most recent and complete study by MKD [7].

The SCF value of the parallel component of the dipole polarizability $\alpha_{zz}$ equals 53.66 with the Pol basis [9,10] and is essentially the same as the result (53.68 a.u.) obtained with the larger HyPol set [26]. The aug-cc-PVTZ set [40] of the size [5s4p3d2f] gives the value of 53.80 a.u., confirming the earlier findings with respect to the performance of the Dunning’s basis sets in calculations of electric dipole polarizabilities. However, one should note that at least at the SCF level of approximation not too much is gained in comparison with the result calculated in much smaller Pol set ([5s3p2d]). The $\alpha_{zz}$ is well described by the bases sets used in the present work. The extensive compilation of different results in the paper by MKD [7] shows only small differences between results obtained with various bases.

For the perpendicular component $\alpha_{xx}$ the overall pattern is similar, although the difference between the Pol and HyPol results becomes slightly larger: 21.39 and 21.79 a.u., respectively. The small discrepancies between our Pol results and the Pol results presented by MKD are due to small differences in geometries used in these two studies. One can see almost perfect agreement between the HyPol and aug-cc-PVTZ results, the difference is less than 0.05 a.u. for the both components of the dipole polarizability tensor.

The electron correlation contribution to $\alpha_{zz}$ is very small and negative. At the most advanced level of our computations, CCSD(T), the result is smaller than the SCF value by 0.25 a.u. for the HyPol and 0.17 a.u. for the Pol basis. The respective contributions obtained by MKD are slightly larger but for all the bases employed are smaller than 0.7 a.u. The electron correlation effect on the perpendicular component...
of the polarizability is small and positive. At the CCSD(T) level of approximation the effect is 0.34 a.u., and 0.46 a.u. for the Pol and HyPol set, respectively. The value reported by MKD reads 0.23 a.u. for the Pol basis.

The results of the MBPT(2) (MP2) calculations are very close to those of the CCSD method. The electron correlation lowers the value of the \( \alpha_{zz} \) component, while increasing slightly the parallel component of the dipole polarizability. The same pattern can be observed in data obtained by MKD. Kobayashi et al. [16] performed CCSD calculations on all isomers of (NC)\(_2\). With the modest cc-PVDZ basis set they obtained considerably underestimated results, in particular for the \( \alpha_{xx} \) component. The results of their MP2 computations with the truncated aug-cc-PVTZ basis set are in good agreement with our data. Fowler and Diercksen [11] used many-body perturbation theory to calculate \( \alpha \) for NCCN using the standard, i.e., segmented Pol basis. The electron correlation contributions obtained in the various orders of perturbation theory were shown to be always small. Also at the full MBPT(4) level the corrections are small and positive.

On the basis of our results and comparisons with other data one can safely conclude that the dipole polarizability \( \alpha \) components are correctly determined and the SCF results for the parallel component obtained with the HyPol basis are less than 1 per cent above the correlated value. For \( \alpha_{xx} \) the correlated value is larger than SCF result by less than 2 per cent of the final correlated value of the dipole polarizability.

For the second hyperpolarizability the only data available for comparison seem to be the recent results of MKD [7]. On passing from Pol to HyPol basis sets one can see significant changes already at the level of the SCF approximation. The HyPol result for \( \gamma_{zzzz} \) is by 500 a.u. (8 per cent) lower than the value obtained with the Pol set. For the \( xxxx \), and \( xxzz \) components this lowering amounts to only 200 a.u. However, this makes as much as 20 per cent of the HyPol value for \( \gamma_{xxzz} \). Let us recall that the Pol basis sets have been shown to generally overestimate the calculated values of the second hyperpolarizability tensor [26]. Also the aug-cc-PVTZ values are systematically lower than the corresponding Pol or HyPol sets. The largest discrepancy occurs for the \( xzzz \) component. The HyPol basis set leads to 2200 a.u. which is to be compared with 1700 a.u. for the aug-cc-PVTZ. The aug-cc-PVTZ basis set is definitely less flexible than the HyPol set, in particular for the \( xxxx \) component. Electron correlation contributions turn out to be quite important for the second hyperpolarizability tensor. The correlation contribution to \( \gamma_{zzzz} \) from the CCSD(T) calculations with the HyPol set amounts to 3200 a.u. (33 per cent of the total value). The corresponding result for the Pol basis set is equal to 3000 a.u. The correlation effects are significantly less important for the \( xxxx \) component: 300 (200) a.u. or 12 per cent (8 per cent) with the HyPol (Pol) set. Similar effect is seen for the off – diagonal component, although in this case the percentage of the correlation contribution is higher: 14 per cent for Pol and 23 per cent for HyPol sets. Since the correlated level calculations with the aug-cc-PVTZ basis become quite demanding the corresponding comparison of the electron correlation contributions is limited only to the MP2 level of approximation. At the MP2 level the Dunning set shows the pattern similar to that observed in calculations with the HyPol or Pol basis sets. There is a large electron correlation effect on the parallel component of the \( \gamma \) tensor, 2900 a.u. (32 per cent), much smaller for the off – diagonal part, 200 a.u. (18 per cent), and none for the \( xxxx \) component. The last result strongly suggests insufficient flexibility of the aug-cc-PVTZ basis set.

The results of the MBPT(2), CCSD and CCSD(T) calculations by MKD [7] are displayed in Table 1. These results have been obtained at the slightly different geometry and using the segmented version of the Pol basis sets. In spite of these differences they agree well with our Pol basis set results. However, they are systematically higher than the present values, i.e. by 560 a.u., 160 a.u., and 70 a.u. for \( zzzz \), \( xxxx \) and
Table 2

Dipole properties of the NCCP molecule\(^a\)). Calculations with Pol and HyPol basis sets and their comparison with the aug-cc-PVTZ results. All values in a.u.

| Basis set      | \(\mu\) \(z\) | \(\alpha\) \(zz\) \(xx\) | \(\beta\) \(zzz\) \(zxx\) | \(\gamma\) \(^b\) \(xxxx\) \(xxzz\) |
|---------------|----------------|------------------|------------------|------------------|
| SCF Pol       | 1.5524         | 93.72            | 36.13            | 198              | 57.5             | 20.5 | 7.3 | 3.6 |
| SCF HyPol     | 1.5581         | 93.71            | 36.50            | 212              | 58.7             | 20.0 | 7.8 | 3.8 |
| SCF aug-cc-PVTZ | 1.5732    | 94.06            | 36.42            | 212              | 60.8             | 19.3 | 5.8 | 3.4 |
| SCF aug-cc-PVQZ\(^c\) | 1.5820     |                  |                  |                  |                  |      |     |     |
| MBPT(2) Pol   | 1.2627         | 90.47            | 35.96            | 85.0             | 53.4             | 29.5 | 8.1 | 4.5 |
| MBPT(2) HyPol | 1.2748         | 90.55            | 36.64            | 103              | 55.8             | 28.9 | 8.7 | 4.5 |
| MBPT(2) aug-cc-PVTZ | 1.2955 | 90.50            | 36.25            | 97.9             | 56.6             | 27.4 | 6.0 | 3.8 |
| MBPT(2) aug-cc-PVQZ\(^c\) | 1.3060     |                  |                  |                  |                  |      |     |     |
| CCSD Pol      | 1.3721         | 89.40            | 35.56            | 100              | 50.8             | 26.4 | 7.6 | 4.1 |
| CCSD HyPol    | 1.3818         | 89.52            | 36.18            | 117              | 51.0             | 25.7 | 8.0 | 4.1 |
| CCSD aug-cc-PVQZ\(^c\) | 1.4170     |                  |                  |                  |                  |      |     |     |
| CCSD(T) Pol   | 1.3199         | 91.30            | 35.81            | 125              | 54.0             | 28.8 | 8.0 | 4.4 |
| CCSD(T) HyPol | 1.3290         | 91.39            | 36.49            | 143              | 54.3             | 28.0 | 8.4 | 4.5 |
| CCSD(T) aug-cc–PVQZ\(^c\) | 1.3570     |                  |                  |                  |                  |      |     |     |

\(^a\) The molecule lies on the \(z\) axis of the coordinate system. Geometry taken from Ref. [21].
\(^b\) The listed results should be multiplied by \(10^3\).
\(^c\) The work of Botchswina and coworkers [21].

**3.2. Electric properties of NCCP**

The results of the present work for the NCCP molecule are presented in Table 2. The knowledge of electric properties of this molecule is very limited. Bizzocchi et al. carried out a careful experimental and computational study on NCCP including the millimeter – wave spectroscopy and CCSD(T) calculations using aug-cc-PVXZ bases [21]. Their values of the dipole moment at the equilibrium bond distance, \(\mu_e\), listed in Table 2, can be compared to our results. At the SCF level both Pol and HyPol agree well with the SCF aug-cc-PVQZ data of Bizzocchi et al.. Our HyPol value (1.5732 a.u.) is smaller by 0.015 a.u. (0.061 D) than the aug-cc-PVQZ result by Bizzocchi et al. [21]. Electron correlation is seen to make significant contributions to the final values of the dipole moment. MBPT(2) calculations lower the SCF value by 0.283 a.u. (HyPol), and 0.278 a.u. for the aug-cc-PVTZ set. As shown by our CCSD(T) calculations, these MBPT(2) results are underestimated. The CCSD(T) HyPol value of 1.329 a.u. is in very good agreement with the accurate aug-cc-PVQZ data and the recommended value for the \(\mu_e\) (1.357 a.u.). The electron correlation contribution amounts to approximately 17 per cent for the HyPol set and can be compared with the value of 16.5 per cent obtained by Bizzocchi et al. with the much larger aug-cc-pVQZ set.

No comparative data on the dipole polarizability and higher – order polarizabilities of NCCP seem to be available. The present dipole polarizability results reveal highly anisotropic character of NCCP with the parallel component \(zz\) being ca. 2.5 times larger than the corresponding \(\alpha_{xx}\) value, independently of the level of theory or the basis set used. The electron correlation contribution behaves similarly as in the case of NCCN. Its overall effect is small and negative for the \(zz\) component (\(-2.32\) a.u. or \(-2.5\) per
cent in CCSD(T) HyPol calculations) and almost negligible for $\alpha_{xx}$ ($-0.01$ a.u., or $-0.03$ per cent for the CCSD(T) method with the HyPol basis set).

The first hyperpolarizability tensor $\beta$ is very difficult to estimate theoretically. Our Pol/HyPol calculations should be treated with caution. The SCF HyPol and aug-cc-PVTZ results for $\beta_{zzz}$ are identical, while the Pol value is lower by 14 a.u., i.e., is less than 7 per cent of the HyPol value. The electron correlation is significant and amounts to about 50 per cent of the final value of $\beta_{zzz}$, leading to the CCSD(T) values of 143 a.u. (HyPol) and 125 a.u. (Pol). The pattern observed for the off – diagonal component $\beta_{xxz}$ is very different. The correlation contribution is relatively small and amounts to 8 per cent in CCSD(T) HyPol calculations. Unlike in the case of the parallel component, the difference between CCSD(T) and MBPT(2) results for $\beta_{xxz}$ is negligible.

Similarly to the case of NCCN the Pol and HyPol values for $\gamma_{zzzz}$ are in close agreement, whereas the values obtained with the aug-cc-PVTZ basis set are systematically lower. The difference between the SCF HyPol result and the aug-cc-PVTZ for the perpendicular component is 2000 a.u., i.e., more than one fourth of the HyPol value. The usefulness of the aug-cc-PVTZ basis set for calculations of the second hyperpolarizability is therefore quite limited. For the usually less demanding $zzzz$ component the discrepancy between Pol/HyPol and aug-cc-PVTZ results is smaller, though again the Dunning set yields lower values of this component.

The electron correlation contribution turns out to be of particular importance for $\gamma_{zzzz}$. The change due to the correlation contribution is 8000 a.u. for the HyPol basis and 8300 for the more compact Pol set. In both cases this makes about 29 per cent of the final value. The MBPT(2) values seem to overestimate the $\gamma_{zzzz}$ component, while CCSD results grossly underestimate it. For the perpendicular $xxxx$ component the electron correlation as computed at the most advanced CCSD(T) level with the HyPol basis is less than 1 a.u. (2 per cent) and is negative. The effect computed at all levels of correlated calculations and for Pol, HyPol and aug-cc-PVTZ basis sets is negligible.

Table 3 displays the calculated electric dipole properties for the PCCP molecule. The geometry of PCCP was optimized at the MP2/6-311G(d,p) level of approximation employing the Gaussian 98 package. The $D_\infty h$ structure is a true minimum with the carbon – carbon and carbon – phosphorus bonds of the length of 1.360 Å, and 1.583 Å, respectively. These values are in good agreement with the QCISD/6-311g(d,p) results of Jones et al. [19]: 1.37 and 1.583 Å, respectively. It should be noted that the carbon–carbon bond in PCCP is shorter than in NCCN by 0.024 Å.

The dipole polarizability tensor $\alpha$ is highly anisotropic with the parallel $zz$ component 3.2 times larger than the perpendicular $xx$ one at the SCF level, and 3.0 times according to the CCSD(T) HyPol calculations. The electron correlation contribution is negative for $\alpha_{zz}$, but unlike in the case of NCCN, is of considerable magnitude: $-12.6$ a.u. or 8 per cent in CCSD(T) calculations with the HyPol basis set. On the other hand, the perpendicular $xx$ component is only slightly affected by taking into account the dynamic electron correlation. The effect computed at the most advanced CCSD(T) level with the HyPol basis is less than 1 a.u. (2 per cent) and is negative. The same negligible effect is found at all levels of correlated calculations and for Pol, HyPol and aug-cc-PVTZ basis sets.

The second hyperpolarizability tensor $\gamma$ is even more anisotropic than the dipole polarizability. For all basis sets used in this study the SCF values of $\gamma_{zzzz}$ exceed 66,000 a.u. and are about 5 times larger
Table 3
Dipole properties of the PCCP molecule. Calculations with Pol and HyPol basis sets and their comparison with the aug-cc-PVTZ results. All values in a.u.

| Basis set     | α       | γ         | γ       | γ         |
|---------------|---------|-----------|---------|-----------|
|               | zz      | xx        | xxxx    | xxxz      |
| SCF Pol       | 171.3   | 53.04     | 67.0    | 15.1      |
|               |         |           |         |           |
| SCF HyPol     | 171.3   | 53.36     | 66.5    | 17.4      |
|               |         |           |         |           |
| SCF aug-cc-PVTZ | 172.1  | 53.25     | 66.2    | 12.3      |
| MBPT(2) Pol   | 156.5   | 52.03     | 99.4    | 16.4      |
|               |         |           |         |           |
| MBPT(2) HyPol | 157.0   | 52.87     | 98.6    | 18.3      |
|               |         |           |         |           |
| MBPT(2) aug-cc-PVTZ | 157.0  | 52.22     | 94.9    | 12.6      |
| CCSD Pol      | 155.4   | 51.37     | 92.4    | 15.1      |
|               |         |           |         |           |
| CCSD HyPol    | 156.0   | 52.09     | 90.9    | 16.7      |
| CCSD(T) Pol   | 158.2   | 51.55     | 94.6    | 15.8      |
|               |         |           |         |           |
| CCSD(T) HyPol | 158.7   | 52.38     | 93.2    | 17.4      |

a) The molecule lies on the z axis of the coordinate system. Geometry optimized at the MP2/6-311G(d,p) level.

b) The listed values are to be multiplied by 10^13.

than γ_{xxxx}. Since the aug-cc-PVTZ is not sufficiently flexible to describe properly the perpendicular components of the second hyperpolarizability the anisotropy becomes higher than for Pol and HyPol sets. The electron correlation increases the parallel component up to 93,200 a.u. (29 per cent of the total correlated value). The MBPT(2) results seem to overestimate γ_{zzzz} which is rather common in the case of very large electron correlation contributions. Compared to the correlation effect on the zzzz component, the electron correlation contribution for γ_{xxxx} is quite modest.

It is worthwhile to mention certain features of the calculated values of the xxxx and xxzz components of γ. The CCSD(T) calculations with the Pol basis yield γ_{xxxx} larger than SCF result 700 a.u., while our presumably best calculations at the CCSD(T) level with the HyPol set show no electron correlation contribution at all. This becomes reversed at CCSD level. The MBPT(2) calculations give a reasonable magnitude of the effect, i.e., the increase by 1300 a.u. with Pol basis sets and by 900 a.u. for the HyPol set. The electron correlation contribution is small and negative for the off – diagonal xxzz component. At the CCSD(T) level the second hyperpolarizability values decrease by 700 a.u. (5 per cent) for HyPol and by 200 a.u. (1 per cent) for Pol sets. Because of the already mentioned insufficient flexibility of the augcc-PVTZ set, the corresponding results for the xxxx and xxzz components of γ are systematically lower than the HyPol values. There seems to be no simple explanation of the observed electron correlation effect on perpendicular components of γ in PCCP. The basis set dependence of these data may only indicate that even the largest HyPol basis sets need to be further augmented.

4. Final conclusions

Electric dipole response properties: dipole polarizability (α), first (β), and second hyperpolarizability (γ) have been systematically studied for three molecules: NCCN, NCCP and PCCP. The parallel zz component of the dipole polarizability increases significantly across this series; from 53.5 a.u. for NCCN to over 158 a.u. for PCCP. The perpendicular component increases less: from 22.2 a.u.(NCCN) to 52.4 a.u. for PCCP. Considering the accuracy of the computational methods used in this work and the performance of the HyPol basis set we are confident that the dipole polarizability α tensor components for all three molecules are accurately determined at the CCSD(T) calculations with the HyPol set. All
systems show quasi – 1D character of the dipole polarizability with the parallel component significantly larger then the \( xx \) component. Electron correlation contribution to the \( \alpha \) tensor for all three systems is very small, this fact can be practically exploited in future calculations of electric properties of longer chains of the conjugated \( \pi \)-systems with CN/CP groups. The usage of the HyPol set seems to be the minimum requirement for obtaining accurate and reliable data for the second hyperpolarizability. In this respect the often used aug-cc-PVTZ basis set turns out to be inadequate. Its further systematic extension in the spirit of the Dunning’s recipe [40] would obviously help. However, this would considerably increase its size.

Similarly to the dipole polarizability of molecules investigated in this study, the second hyperpolarizability is also a highly anisotropic, quasi – 1D property. The value of the \( zzzz \) component increases approximately ten times; from 9000 a.u. for NCCN to 93,000 a.u. for the PCCP molecule. The increase for the \( xxxx \) component is far less dramatic: from 2500 a.u. (NCCN) to 15800 a.u. for PCCP. The dynamic electron correlation effects are important for this property, generally their contribution is significantly large and positive for the \( zzzz \) component and much smaller for the other two components. It also follows from the present study that realistic calculations of the second hyperpolarizability require very careful incorporation of the correlation effects. Moreover, to improve upon the reliability of the calculated values for perpendicular components of \( \gamma \) one should further explore the basis set effects.

The data in Table 1 to 3 are given in atomic units, the most convenient from the computational point of view. For the dipole polarizability \( \alpha \) 1 a.u. equals \( 1.6488 \cdot 10^{-41} \) \( C^2 m^2 J^{-1} \), for the \( \beta \) hyperpolarizability 1 a.u. equals \( 3.2064 \cdot 10^{-53} \) \( C^3 m^3 J^{-2} \), while for the second-hyperpolarizability tensor \( \gamma \) the conversion factor reads \( 6.2354 \cdot 10^{-65} \) \( C^4 m^4 J^{-3} \).

Acknowledgements

Part of the computations were performed at the Computational Center of the Silesian University of Technology, Gliwice in the framework of the supported project ‘Theoretical determination of molecular electric and optical properties’. The authors wish to thank Professor Andrzej J. Sadlej of the Nicolaus Copernicus University, Toruń, Poland, for helpful discussions and interest in this project.

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