ELECTRIC PROPERTIES OF CYANOBORANE ISOMERS

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Dedicated to Professor Josef Paldus on the occasion of his 70th birthday.

Cyanoborane isomers and their acyclic and cyclic oligomers serve as useful models for studying properties of molecules with alternating electron-rich and electron-deficient groups. Static electric properties including electronic dipole moment, polarizability, first and second hyperpolarizabilities of three stable isomeric monomers – boranylmethanenitrile, borazirene and 1-(methanylidyne)borazan-1-ium-2-ide – have been calculated at the MP2, CCSD and CCSD(T) levels using various basis sets. In addition, frequency-dependent (hyper)-polarizabilities of the most stable isomer have been evaluated via the CCSD response theory.

Keywords: Electric properties; Electron correlation; Complete basis set limit; Cyanoboranes; Dipole moment; Polarizability; CCSD; *Ab initio* calculations.

Cyanoborane isomers[1–4] and their acyclic and cyclic oligomers[5–9] serve as useful models for studying properties of molecules with alternating electron-rich and electron-deficient groups. The backbone of these systems is B–C–N or B–N–C sequence that can be further altered by suitable electron-withdrawing/electron-donating substituents to gain models for conducting polymers or push-pull systems. The smallest members of this series are three isomers **1**–**3**.

Cyanoborane **1** is experimentally known. IR and NMR spectra of this species were first reported by Spielvogel[1]. One interesting property of **1** is its ability to oligomerize, forming macrocycles with relatively isolated islands C≡N bridged together with electron deficient BH_2 groups[8]. Alternatively,

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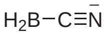
one can consider also rings containing just repeating [–C=N–] units with exocyclic BH_2 groups. Structure **2**, borazirene, belongs to the group of smallest aromatic systems being isoelectronic with aromatic three-membered rings, such as $C_3H_3^+$ or C_3H_2. We investigated its aromatic properties[10] studying ring currents for a series of small aromatic systems.


$H_2B-C\equiv\bar{N}$

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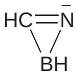

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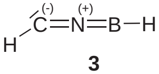

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In our previous computational study[4] we have found that aromatic ring **2** lies ≈70 kJ/mol above **1** and that the path from **1** to **2** is symmetry-forbidden (the pertinent transition state was too high, with the barrier higher than 250 kJ/mol). This barrier turned out to be significantly lower for the anion $HBCN^-$ (131 kJ/mol)[11]. There is a considerable charge transfer from HCN to BH in structure **3**, thus it is a mixture of a charge transfer complex and chemically bound molecule. We limit ourselves to closed-shell species though we are aware that triplet for structure **3** could probably compete with the singlet[7]. There is only limited knowledge of electric properties (polarizabilities) of dimers of these systems[6], data for monomers are completely missing.

It has been suggested that oligomers and polymers built from asymmetric units could be of interest for nonlinear optical (NLO) applications because they can exhibit first hyperpolarizabilities per unit length of magnitude similar to the best donor/acceptor (D/A) systems[12]. In particular, investigations of polymethineimine (PMI) oligomers have shown[13] that for sufficiently large oligomers, β^{e}_{L}/N is similar to $|\beta^{e}_{L}/N|_{max}$ of NH_2/NO_2^--substituted polyene chains, and the specific chain-length dependence of β^{e}_{L}/N can be rationalized in terms of unit cell and chain asymmetries. In this context, the nature of backbone atoms can be varied to optimize the NLO response. Greater atomic alternation (i.e. the difference between the atoms) within a given row of the Periodic Table is associated with a decrease in electron delocalization. This is usually detrimental to β^{e}_{L} (ref.[14]) but, at the same time, such alternation creates the backbone asymmetry that is responsible for non-zero β^{e}_{L} in the first place. Therefore, it was proposed[12] to investigate other asymmetric unit cell oligomers and polymers containing B–C and B–N bonds in order to span new regions of delocalization-asymmetry space. The study of linear boron–nitrogen chains[15] appears to be topical in this context.

The principal motivation for this study was therefore to obtain a deeper insight into those aspects of electronic structure of selected closed-shell

B/C/N monomers that are related to static and frequency-dependent electric and optical properties as well as to test the sensitivity of the properties with respect to the choice of an appropriate correlated approach and basis sets. An additional goal was to compare applicability of various complete basis set (CBS) schemes for obtaining molecular properties with the R12 approach.

THEORETICAL AND COMPUTATIONAL ASPECTS

Definition of Electric Properties

If a molecule is exposed to external static and/or dynamic electric fields ($\vec{F}$), the field-dependence of its dipole moment can be described by a Taylor series[16,17]

$$\begin{aligned}\mu_\alpha(\omega_\sigma) = \mu_\alpha^0 &+ \sum_\beta \alpha_{\alpha\beta}(-\omega_\sigma;\omega_1)F_\beta(\omega_1) + \\ &+ \frac{1}{2}K^{(2)}\sum_{\beta\gamma}\beta_{\alpha\beta\gamma}(-\omega_\sigma;\omega_1,\omega_2)F_\beta(\omega_1)F_\gamma(\omega_2) + \ldots \\ &+ \frac{1}{6}K^{(3)}\sum_{\beta\gamma\delta}\gamma_{\alpha\beta\gamma\delta}(-\omega_\sigma;\omega_1,\omega_2,\omega_3)F_\beta(\omega_1)F_\gamma(\omega_2)F_\delta(\omega_3) + \ldots \end{aligned} \tag{1}$$

where the $K^{(n)}$ factors are such that the nonlinear responses converge towards the same static limit. The numbers in parentheses ($-\omega_\sigma$; ω_1, ω_2, ω_3), with $\omega_\sigma = \sum_i \omega_i$ are the frequencies of the oscillating electric fields (in the order F_β, F_γ, F_δ, ...). The summations run over the field indices β, γ, and δ associated with the Cartesian coordinates. μ_α^0 is the α-component of the permanent dipole moment and $\alpha_{\alpha\beta}(-\omega_\sigma;\omega_1)$ is the αβ-component of the dynamic dipole polarizability tensor. The second-order NLO quantities, including the static first hyperpolarizability, the dc-Pockels effect, the second harmonic generation (SHG), and the optical refractivity (OR) are then given by $\beta(0;0,0)$, $\beta(-\omega;\omega,0)$, $\beta(-2\omega;\omega,\omega)$, and $\beta(0;\omega,-\omega)$, respectively. The third-order NLO quantities including the static second hyperpolarizability, dc-Kerr effect, electric field-induced second harmonic generation (ESHG), third harmonic generation (THG), and degenerate four-wave mixing (DFWM) responses are given by $\gamma(0;0,0,0)$, $\gamma(-\omega;\omega,0,0)$, $\gamma(-2\omega;\omega,\omega,0)$, $\gamma(-3\omega;\omega,\omega,\omega)$, and $\gamma(-\omega;\omega,-\omega,\omega)$, respectively. Within the Born–Oppenheimer approximation, the electric properties as defined above can be decomposed into the electronic, vibrational and rotational parts. In this study we focus on the electronic contribution though, in line with recent theoretical investigations of small and medium-size conjugated organic molecules[12,18], the vibrational part of hyperpolarizabilities can be expected to be comparable with the former. Clearly, both components (electronic and vibrational) should be taken into account for accurate estimations of the total values. Experimental techniques usually do not enable determining the particular elements of the (hyper)polarizability tensors. Measurable quantities can be defined with respect to the permanent molecular dipole moment placed along the z-axis as parallel ($\beta_{||}$ and $\gamma_{||}$) and perpendicular ($\beta_{\perp}$ and $\gamma_{\perp}$) static hyperpolarizabilities in the following manner[16,19]:

$$\beta_{||} = 3\beta_{\perp} = \frac{3}{5}\sum_{\xi}\beta_{\xi\xi z} \tag{2}$$

and

$$\gamma_{||} = 3\gamma_{\perp} = \frac{1}{5}\sum_{\xi\eta}\gamma_{\xi\xi\eta\eta} \; . \tag{3}$$

Their combination leads to the anisotropies associated with the Kerr effect, defined as $\beta^{K} = 3/2(\beta_{||} - \beta_{\perp})$ and $\gamma^{K} = 3/2(\gamma_{||} - \gamma_{\perp})$, respectively. For the static limit, it implies that $\beta^{K} = \beta_{||}$ and $\gamma^{K} = \gamma_{||}$. Analogous formulae can be defined for the frequency-dependent NLO quantities. For example, the parallel components of the hyperpolarizabilities associated with the dc-Pockels and the dc-Kerr effects, respectively, are given as follows:

$$\beta_{||}(-\omega;\omega,0) = \frac{1}{5}\sum_{\xi}\left(\beta_{\xi\xi z}(-\omega;\omega,0) + 2\beta_{z\xi\xi}(-\omega;\omega,0)\right) \tag{4}$$

and

$$\gamma_{||}(-\omega;\omega,0,0) = \frac{1}{15}\sum_{\xi\eta}\left(\gamma_{\xi\xi\eta\eta}(-\omega;\omega,0,0) + 2\gamma_{\xi\eta\xi\eta}(-\omega;\omega,0,0)\right) . \tag{5}$$

Methods

The presence of multiple bonds in the investigated systems makes their theoretical study sensitive to the inclusion of electron correlation. In this study we limit ourselves to a hierarchy of correlation methods starting from the second order Møller–Plesset perturbation scheme (MP2)[20], through the coupled cluster (CC) theory[21–28] with single and double excitations (CCSD)[29] up to approximate inclusion of triple excitations within the

CCSD(T) [30,31]. Despite its relative simplicity, the MP2 often recovers a substantial part of the electron correlation effects. Nevertheless, for more accurate predictions of molecular properties of small many electron systems the CC approach has been proved superior. Since its original formulation by Čížek[21,22], many variants of the CC method have emerged[24–28] and it became soon clear that for accurate calculations the effect of triple excitations has to be accounted for. Among the methods doing so, the CCSD(T) plays a prominent role, as a successful approximation to much more expensive full inclusion of triple excitations within the CCSDT. In the CCSD(T), the triple excitation contribution to the energy is calculated in a single step as in the fourth-order perturbation theory but using final CCSD amplitudes instead of second-order ones[32]; in addition, a fifth-order term coupling the single excitations with triple excitations is included[30]. Needless to stress that the size-extensivity, as a fundamental property of (most) CC theories can be of importance when the size of the system increases, e.g. in the study of cyanoborane oligomers and polymers.

At the RHF level, the electronic dipole moment and static (hyper)-polarizability tensor components have been calculated analytically via the random phase approximation[33,34]. The “relaxed-orbital” MP2, CCSD, and CCSD(T) energy derivatives have been obtained numerically by a Romberg-type procedure[15,35] based on the finite difference scheme using lower-order properties (energy and/or dipole moment) determined at different field amplitudes. Numerical accuracy can be estimated from the convergence with respect to the number of points taken into account. After testing the numerical stability of our results we have used the electric field intensities of 0, ±0.0016, ±0.0032, ±0.0064, ±0.0128, and ±0.0256 a.u. With this approach, the numerical accuracy of usually less than ±10 a.u. for the reported static electronic second hyperpolarizabilities has been achieved, except for the longitudinal R12 and HyPOL γ values, whose uncertainty is ±100 a.u. For other properties, the numerical uncertainty is below the reported precision.

Since the frequency-dependent polarizabilities and hyperpolarizabilities rather than their static counterparts are more appropriate for comparison with experiment, the frequency dispersion of the properties has been studied at the CCSD level within the coupled cluster linear[36], quadratic[37] and cubic[38] response theory. It is known[39] that many of the standard electron correlation methods (including the MP2 and CCSD(T) approaches) are not best suited for calculating of frequency-dependent molecular properties due to incorrect pole structure, despite accurate results that can be obtained with these methods for static properties. On the other hand, an adequate description of electronic excitation energies leading to accurate predictions of dynamic properties is obtained using higher members of the hierarchy of CC models such as CCSD and CC3[40–43]. In the frequency-independent limit, these approaches coincide with the so-called orbital-unrelaxed energy derivatives. Comparison of orbital-relaxed and unrelaxed CC approaches provided by Salter et al.[44], Christiansen et al.[45], Larsen et al.[46] and Hättig and Jørgensen[47] for a small series of atomic and diatomic systems suggests that (i) though they give quite different results for static polarizabilities and first hyperpolarizabilities, there is no clear preference for either choice; however, (ii) the unrelaxed approach is theoretically preferable for the calculation of frequency-dependent properties.

The dynamic polarizabilities, the second-order NLO properties associated with the dc-Pockels, SHG and OR processes, and the third-order NLO properties associated with the dc-Kerr, THG and DFWM processes have been evaluated at the following frequencies: 0.0 (static), 0.06562487 a.u. (corresponding to a wavelength of 694.3 nm) and 0.07200276 a.u. (corresponding to 632.8 nm). In the low-frequency region of the spectrum the expansion formulas for the frequency dispersion of the diagonal as well as the average quantities can be derived.

Basis Sets

It is well known that the basis set requirements for obtaining a certain accuracy of a given molecular property are usually different from those required for a corresponding accuracy in energy and/or molecular geometry. It has been shown for small systems[48–50] that for accurate evaluation of (hyper)-polarizabilities the use of diffuse and polarization basis functions is inevitable. We have considered correlation-consistent polarized valence cc-pVTZ and cc-pVQZ sets[51] as the bases generally considered appropriate for obtaining accurate equilibrium geometry parameters. Then, the first three members of the augmented series, aug-cc-pV*X*Z[51,52], have been used in calculations of linear as well as non-linear molecular properties. These basis sets are expected to be more flexible in responding to the external field than non-augmented counterparts due to the presence of highly diffuse functions. There is wide evidence[45,47,53–55] that in particular for the atomic second hyperpolarizabilities, f functions are crucial already at the SCF level. For molecules with two- or three-dimensional structure, however, the f functions appear to be less important for γ and reasonable estimates can be obtained already with the aug-cc-pVDZ[47]. Finally, the Sadlej Pol basis sets[56,57] and the second-order polarized HyPol basis sets[58], have been applied. Though smaller Pol basis sets have been proposed for calculations of electric dipole moments and dipole polarizabilities, they were also found to be a reasonable choice for calculations of first hyperpolarizabilities of small polyatomic molecules[59–61]. The extended HyPol is a purpose-built basis set proposed for evaluation of hyperpolarizabilities. However, from our previous experience[50], which is in agreement with other theoretical observations[12], it turns out that this basis set is often difficult to apply to small (in particular linear) conjugated systems due to convergence difficulties related mostly to linear dependences.

In order to determine the reliability, we confront the results with those obtained by using larger sets and/or we estimated complete basis set limit (CBS) either using extrapolations or the explicitly correlated R12 approach.

Most extrapolation techniques towards the CBS limit described in the literature[62–71] concern extrapolations of the energy or quantities directly related to the energy. Different extrapolation formulae are frequently used for the RHF part of the total energy, while the correlation contribution is treated separately. Detailed discussion of various extrapolation techniques and physical reasoning for using specific formulae do not need to be repeated here.

Within the calculations using correlation-consistent basis sets with different cardinal numbers X, an established approach for obtaining estimations of the CBS limits for the molecular energies is provided by a separate extrapolation of the Hartree–Fock energy as suggested by Feller[72,73]

$$E_{\mathrm{RHF}}(X) = E_{\mathrm{RHF}}^{\mathrm{CBS}} + \frac{a}{\exp(cX)} \qquad (6)$$

and using two-point extrapolation formula proposed by Helgaker and co-workers[65,66] for the correlation energy

$$E_{\mathrm{corr}}(X) = E_{\mathrm{corr}}^{\mathrm{CBS}} + \frac{b}{X^{3}}\ . \qquad (7)$$

We remind that the cardinal number X is directly related to the highest angular momentum basis function. X = 2 and 3 for double- and triple-zeta sets, respectively. The coefficient c in Eq. (6) was set to unity due to two-point extrapolations that we perform from aug-cc-pVXZ (X = D, T and T, Q) results.

Let us stress, however, that there is no straightforward justification for the use of such an approach directly to properties that depend on the energy nonlinearly, like electric properties treated in this paper. Therefore, we have employed various strategies to obtain the extrapolated property values. If one uses the finite field calculation, the energies can be extrapolated for all field strengths and the final property calculated from these extrapolated energies. We denote such results by CBS-A1. Alternatively, one can assume validity of Eqs (*6*) and (*7*) for the individual properties, too. In this case E has to be replaced by μ, α, β or γ in those equations. Such values will be referred to as CBS-A2. It should be noted that only the latter approach is applicable for obtaining the CBS values of frequency-dependent properties.

We have also applied seemingly more crude empirically based formula advocated by Zahradník[74] which simply relates the energy with the number of basis functions N_{BAS}

$$E(N_{\mathrm{BAS}}) = E^{\mathrm{CBS}} + \frac{d}{N_{\mathrm{BAS}}} \, . \qquad (8)$$

Equation (*8*) is in close relation to Eq. (*7*) for the correlation-consistent basis sets[65,75], but it roughly works for different types of basis set series. The extrapolated property values using this formula will be denoted CBS-B1 and CBS-B2, respectively, for the results obtained from extrapolated field-dependent energies or directly extrapolated properties.

In order to assess the quality of the basis sets used for evaluation of molecular properties, we have also performed explicitly correlated MP2 calculations using the so-called R12 approach[76] in approximation B, MP2-R12/B [77,78] which is a more rigorous alternative to formerly proposed MP2-R12 variants[79,80]. The R12 approach provides properties close to the CBS limits[81], but the used basis sets must still be fairly extensive and saturated for lower angular momenta. In this study we have used the R12-optimized 9s6p4d set for hydrogen[82], and 19s14p8d6f4g sets (and their spdf subsets) for atoms B, C, N (refs[83,84]). MP2-R12/B calculations of the dipole moment and the longitudinal component of (hyper)polarizabilities have been carried out using the MP2 (frozen core)/aug-cc-pVTZ optimized geometries.

RESULTS AND DISCUSSION

Most of the geometry optimizations as well as of the molecular property calculations reported in this study used the Dalton quantum chemistry program suite[85]. CCSD(T)/cc-pVQZ optimizations employed the ACES2 package[86] and the R12 calculations were carried out using the recent version of DIRCCR12-OS code[87].

Of course, electric properties are strongly dependent on the molecular geometry parameters. Therefore, we start our discussion with the analysis of the basis set dependence of molecular geometry of the investigated cyanoborane monomers. In the second paragraph various aspects of extrapolating the electric property values to the CBS limits within the aug-cc-pV*X*Z series are discussed. The third section is focused on testing the sensitivity of the properties to the accuracy of geometry parameters. The next paragraph contains a comparison of different electron correlated methods. Finally, for the most stable isomer, H_2BCN, we present also results for frequency-dependent linear and nonlinear optical properties.

Basis Set Dependence of Molecular Geometry

Molecular geometries of the investigated cyanoborane isomers optimized at various levels of theory and basis sets are presented in Tables I–III. These data are compared with the DFT-B3LYP/DZP and CCSD(T)/cc-pVTZ structures obtained by Gregušová et al.[7,8].

Results for all the three molecular systems obtained at the uniform correlated level show that

TABLE I
The basis set dependence of geometry parameters for H_2BCN (bond lengths in Å, angles in °)

Method	Basis set	Type of basis	*r*(CB)	*r*(NC)	*r*(HB)	∠HBH
MP2[a]	DZP (Dunning)	4.2.1/2.1 (55)	1.5451	1.1905	1.1830	122.98
MP2[a]	cc-pVTZ	4.3.2.1/3.2.1 (108)	1.5340	1.1735	1.1824	122.19
MP2[a]	aug-cc-pVDZ	4.3.2/3.2 (87)	1.5506	1.1892	1.1964	122.50
MP2[a]	aug-cc-pVTZ	5.4.3.2/4.3.2 (184)	1.5353	1.1738	1.1826	122.32
DFT-B3LYP[b]	DZP (Dunning)	4.2.1/2.1 (55)	1.5369	1.1702	1.1895	118.68
CCSD(T)[a,b]	cc-pVTZ	4.3.2.1/3.2.1 (108)	1.5363	1.1674	1.1856	118.82
CCSD(T)[a]	cc-pVQZ	5.4.3.2.1/4.3.2.1 (225)	1.5345	1.1637	1.1845	118.75

[a] Inner-shell electrons were not correlated. [b] Taken from ref.[7]

TABLE II
The basis set dependence of geometry parameters for HCNBH (open form) (bond lengths in Å, angles in °)

Method	Basis set	Type of basis	*r*(HC)	*r*(CN)	*r*(BH)	*r*(NB)	∠HCN	∠CNB	∠HBN
MP2[a]	DZP Dunning	4.2.1/2.1 (55)	1.1118	1.3168	1.1607	1.2877	106.86	173.18	179.42
MP2[a]	cc-pVTZ	4.3.2.1/3.2.1 (108)	1.1062	1.3016	1.1642	1.2777	107.68	172.92	179.45
MP2[a]	aug-cc-pVDZ	4.3.2/3.2 (87)	1.1206	1.3180	1.1746	1.2862	107.24	172.16	179.72
MP2[a]	aug-cc-pVTZ	5.4.3.2/4.3.2 (184)	1.1061	1.3007	1.1647	1.2787	107.96	172.97	178.95
DFT-B3LYP[a,b]	DZP Dunning	4.2.1/2.1 (55)	1.117	1.298	1.165	1.285	109.05	173.40	178.80
CCSD(T)[a]	cc-pVTZ	4.3.2.1/3.2.1 (108)	1.1039	1.3007	1.1654	1.2722	108.00	173.23	179.44
CCSD(T)[a]	cc-pVQZ	5.4.3.2.1/4.3.2.1 (225)	1.1091	1.3035	1.1665	1.2731	107.87	172.53	179.62

[a] Inner-shell electrons were not correlated. [b] Taken from ref.[7]

TABLE III
The basis set dependence of geometry parameters for borazirene (bond lengths in Å, angles in °)

Method	Basis set	Type of basis	*r*(HC)	*r*(CN)	*r*(BH)	*r*(BN)	∠HCN	∠CNB	∠HBC
MP2[a]	DZP Dunning	4.2.1/2.1 (55)	1.0857	1.3363	1.1702	1.4561	129.68	62.82	160.19
MP2[a]	cc-pVTZ	4.3.2.1/3.2.1 (108)	1.0806	1.3210	1.1729	1.4457	129.76	62.88	160.69
MP2[a]	aug-cc-pVDZ	4.3.2/3.2 (87)	1.0934	1.3356	1.1853	1.4604	129.71	63.01	160.73
MP2[a]	aug-cc-pVTZ	5.4.3.2/4.3.2 (184)	1.0813	1.3203	1.1734	1.4465	129.87	62.94	161.04
DFT-B3LYP[b]	DZP Dunning	4.2.1/2.1 (55)	1.0929	1.3195	1.1762	1.4487	129.58	63.46	160.94
CCSD(T)[a]	cc-pVTZ	4.3.2.1/3.2.1 (108)	1.0829	1.3202	1.1764	1.4462	129.86	62.98	160.76
CCSD(T)[a]	cc-pVQZ	5.4.3.2.1/4.3.2.1 (225)	1.0823	1.3150	1.1756	1.4400	129.95	63.08	161.02

[a] Inner-shell electrons were not correlated. [b] Taken from ref.[7]

1. the differences between the DZP and aug-cc-pVTZ optimum geometry parameters are not negligible; typically they are of about 0.005 Å, but they reach 0.017 Å for *r*(CN) in HCNBH (open form) and 0.020 Å for *r*(CB) in H_2BCN;

2. the cc-pVTZ and aug-cc-pVTZ basis sets provide very similar geometries and thus both can be considered acceptable;

3. CCSD(T)/cc-pVTZ and CCSD(T)/cc-pVQZ geometries are very close (the differences do not exceed ±0.5% for both bond lengths and bond angles) indicating that the CCSD(T)/cc-pVTZ geometries are fairly stable;

4. the geometries obtained with the aug-cc-pVDZ basis set seem to be inaccurate.

Comparison of MP2 results with the DFT-B3LYP and CCSD(T) values reveals that the MP2 tends to slightly underestimate the length of bonds containing a hydrogen atom and to overestimate all other types of bonds. Similarity of the cc-pVTZ and aug-cc-pVTZ results at the MP2 level supports our use of the CCSD(T) geometries obtained with the former basis for the final evaluation of electric properties of the investigated systems.

Basis Set Dependence of Electric Properties

In Tables IV–VI MP2/aug-cc-pV*X*Z results and estimations of the CBS limits for the longitudinal components of electric property tensors obtained with the techniques described in Section Basic Sets are compared with the reference MP2-R12/B values. The reported values are related to the molecules placed in the *x*–*z* plane with the dipole moment along the *z*-axis as shown in Fig. 1.

It can be seen that for lower-order properties (μ and α) reasonable estimates can be obtained even with aug-cc-pVDZ basis sets, with an error within 2%. A similar behavior of aug-cc-pVDZ has been observed in the case of acetonitrile[88]. Increasing the size of the basis set within the single augmented cc-pV*X*Z series leads to decrease in the error (up to 0.5% for aug-cc-pVQZ). As expected for the POL basis set, which is of similar size and diffuse properties as aug-cc-pVDZ, the differences in the dipole moment and polarizability values are also small. It is known[58,60,89] that for the low-order properties, the HyPOL basis set provides results very close to those obtained with the smaller Sadlej basis set. This was also observed in our case.

In accord with previous studies[45–47] on the importance of f- and g-type functions within the augmented cc-pV*X*Z series for evaluation of molecular first hyperpolarizability, dramatic improvement of the results in a sequence DZ → TZ → QZ can be observed for all the three molecules. Although the error with the smallest basis set for borazirene reaches as much as 44%, having in mind the small magnitude of the reference value for β_{zzz} (–9.4 a.u.), it can still be concluded that aug-cc-pVDZ provides qualitatively correct estimations of β for molecules with a similar nature of chemical bonds. The performance of POL basis sets appears to be quite inconsistent. Even for the larger basis set containing f-type functions the quality of the results remains at the aug-cc-pVDZ level for the noncyclic isomers.

For the second hyperpolarizability it was found that within the aug-cc-p*VX*Z series the predicted values increase in the order DZ < TZ < QZ. While aug-cc-pVDZ underestimates the reference value obtained with R12-spdfg, aug-cc-pVTZ provides results very close (within 2.5%) to the reference value. The aug-cc-pVQZ basis set slightly overshoots these values. POL basis set leads to an overestimation of the reference values by about 5–10%. The HyPOL basis set provides the results of similar quality as the smaller POL basis, but it should be mentioned that the convergency problems deteriorate the numerical accuracy of the results, which also disabled the evaluation of γ_{zzzz} for an open form of HCNBH.

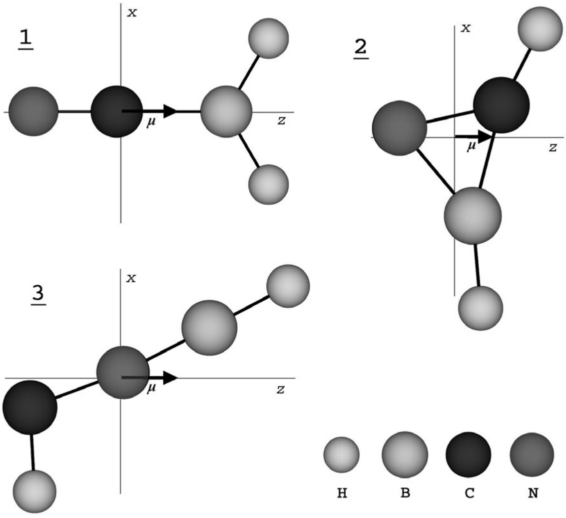

FIG. 1

Schematic illustration of the molecular structures of boranylmethanenitrile (**1**), borazirene (**2**), and 1-(methanylidyne)borazan-1-ium-2-ide – an open form of borazirene (**3**) in order to identify the tensor components of their electric properties. The molecules are placed in the *x*–*z* plane with the dipole moment along the *z*-axis.

Concerning the extrapolation techniques one can observe the following. Though there are small differences between schemes 1 and 2 for higher-order properties, both extrapolated field dependent energy derivatives (scheme 1) and direct extrapolations of the properties (scheme 2) give very similar if not identical results. For dipole moments and polarizabilities both CBS-A and CBS-B schemes using the aug-cc-pV*X*Z (*X* = D, T an *X* = T, Q) basis sets lead to results within 1% error from the reference values. The best

TABLE IV
Estimations of the CBS limits and comparison with the R12 values for longitudinal properties (in a.u.) of H_2BCN in MP2 (frozen core)/aug-cc-pVTZ geometry. CBS limits are extrapolations from aug-cc-pV*X*Z (*X* = D, T and T, Q) results

Method	Basis	μ	α_{zz}	β_{zzz}	γ_{zzzz}
RHF	aug-cc-pVDZ	1.2502	41.688	–80.5	6033
	aug-cc-pVTZ	1.2453	41.691	–78.7	6333
	aug-cc-pVQZ	1.2452	41.676	–78.5	6434
MP2	aug-cc-pVDZ	1.1102	41.932	–71.0	8201
	aug-cc-pVTZ	1.1175	41.793	–69.1	8447
	aug-cc-pVQZ	1.1222	41.707	–68.0 ± 1.0	8650 ± 50
	Pol (Sadlej)	1.1043	41.978	–65.9	8919
	HyPol (Sadlej)	1.1070	41.969	–70.0	8763 ± 20
	CBS (X = D,T)-A1[a]	1.1197	41.735	–68.1	8601
	CBS (X = D,T)-B1[b]	1.1240	41.668	–67.5	8672
	CBS (X = D,T)-A2[c]	1.1198	41.738	–65.5	9025
	CBS (X = D,T)-B2[d]	1.1240	41.668	–67.4	8668
	CBS (X = T,Q)-A1[a]	1.1227	41.690	–67.8 ± 0.3	8723 ± 50
	CBS (X = T,Q)-B1[b]	1.1281	41.601	–66.6 ± 0.4	8904 ± 100
	CBS (X = T,Q)-A2[c]	1.1227	41.690	–67.8	8721
	CBS (X = T,Q)-B2[d]	1.1280	41.601	–66.6	8902
MP2-R12/B	R12 spdf/spd	1.1281	41.601	–67.9	8474
	R12 spdfg/spd	1.1280	41.615	–68.0	8438

[a] Numerical derivatives of field dependent energies extrapolated according to Eqs (*6*) and (*7*). [b] Numerical derivatives of field dependent energies extrapolated according to Eq. (*8*). [c] Extrapolations of the pertinent property values according to equations analogous to Eqs (*6*) and (*7*). [d] Extrapolations of the pertinent property values according to equation analogous to Eq. (*8*).

estimates (within an error of 0.1%) for these properties have been obtained with Zahradník's scheme CBS-B (X = T, Q). With increasing order of the response property the accuracy of the extrapolations deteriorates, though for β it remains within about 2% for the CBS-B (X = T, Q) scheme. Thanks to the overestimation of γ_{zzzz} when using the aug-cc-pVQZ basis set, the CBS (X = T, Q) schemes overshoot the reference values. Pragmatically, the aug-cc-pVTZ values can then be viewed as very good estimates for the second hyperpolarizabilities.

TABLE V
Estimations of the CBS limits and comparison with the R12 values for longitudinal properties (in a.u.) of HCNBH (open form) in MP2 (frozen core)/aug-cc-pVTZ geometry. CBS limits are extrapolations from aug-cc-pVXZ (X = D, T and T, Q) results

Method	Basis	μ	α_{zz}	β_{zzz}	γ_{zzzz}
RHF	aug-cc-pVDZ	1.3215	52.446	–174.8	31933
	aug-cc-pVTZ	1.3313	52.509	–181.7	33438
	aug-cc-pVQZ	1.3308	52.518	–178.2	34448
MP2	aug-cc-pVDZ	1.1395	58.702	–170.5	44302
	aug-cc-pVTZ	1.1457	58.768	–189.8	45450
	aug-cc-pVQZ	1.1471	58.621	–186.7	47363 ± 500
	Pol (Sadlej)	1.1279	58.800	–173.1	49827 ± 100
	HyPol (Sadlej)	1.1207	58.557 ± 0.005	–162.4	–
	CBS (X = D,T)-A1[a]	1.5000	58.838	–199.2	46186
	CBS (X = D,T)-B1[b]	1.1513	58.827	–207.0	46520
	CBS (X = D,T)-A2[c]	1.1499	58.806	–199.0	46176
	CBS (X = D,T)-B2[d]	1.1513	58.827	–207.1	46480
	CBS (X = T,Q)-A1[a]	1.1470	58.608	–184.8	47598 ± 500
	CBS (X = T,Q)-B1[b]	1.1487	58.439	–183.1	48794 ± 800
	CBS (X = T,Q)-A2[c]	1.1470	58.608	–184.7	48057 ± 500
	CBS (X = T,Q)-B2[d]	1.1488	58.438	–182.8	49741 ± 800
MP2-R12/B	R12 spdf/spd	1.1491	58.451	–185.4	45064 ± 300
	R12 spdfg/spd	1.1499	58.454	–185.6	45051 ± 200

[a] Numerical derivatives of field dependent energies extrapolated according to Eqs (*6*) and (*7*). [b] Numerical derivatives of field dependent energies extrapolated according to Eq. (*8*). [c] Extrapolations of the pertinent property values according to equations analogous to Eqs (*6*) and (*7*). [d] Extrapolations of the pertinent property values according to equation analogous to Eq. (*8*).

A comparison of the R12-B/spdf and R12-B/spdfg results reveals that already the smaller R12 basis set is saturated enough to provide very accurate linear as well as nonlinear properties.

Geometry Dependence of Electric Properties

In order to see the sensitivity of electric properties of cyanoborane monomers to geometry changes we have performed MP2/aug-cc-pVDZ calcula-

TABLE VI
Estimations of the CBS limits and comparison with the R12 values for longitudinal properties (in a.u.) of HCNBH (cyclic form) in MP2 (frozen core)/aug-cc-pVTZ geometry. CBS limits are extrapolations from aug-cc-pV*X*Z (*X* = D, T and T, Q) results

Method	Basis	μ	α_{zz}	β_{zzz}	γ_{zzzz}
RHF	aug-cc-pVDZ	0.7631	29.586	–6.3	3827
	aug-cc-pVTZ	0.7620	29.634	–5.9	4313
	aug-cc-pVQZ	0.7618	29.630	–5.8	4510
MP2	aug-cc-pVDZ	0.7080	30.084	–5.3	6661
	aug-cc-pVTZ	0.7110	29.988	–7.7	7309
	aug-cc-pVQZ	0.7141	29.929	–8.5	7570 ± 20
	Pol (Sadlej)	0.7088	30.046	–12.5	7920
	HyPol (Sadlej)	0.7079	30.187	–8.3	7996 ± 20
	CBS (X = D,T)-A1[a]	0.7121	29.949	–8.6	7656
	CBS (X = D,T)-B1[b]	0.7136	29.902	–9.8	7885
	CBS (X = D,T)-A2[c]	0.7121	29.955	–8.1	8350
	CBS (X = D,T)-B2[d]	0.7137	29.902	–9.9	7890
	CBS (X = T,Q)-A1[a]	0.7144	29.920	–8.6	7692
	CBS (X = T,Q)-B1[b]	0.7180	29.856	–9.6	7896
	CBS (X = T,Q)-A2[c]	0.7144	29.920	–8.6	7692
	CBS (X = T,Q)-B2[d]	0.7179	29.856	–9.5	7894
MP2-R12/B	R12 spdf/spd	0.7174	29.861	–9.2	7457
	R12 spdfg/spd	0.7175	29.859	–9.4	7494

[a] Numerical derivatives of field dependent energies extrapolated according to Eqs (*6*) and (*7*). [b] Numerical derivatives of field dependent energies extrapolated according to Eq. (*8*). [c] Extrapolations of the pertinent property values according to equations analogous to Eqs (*6*) and (*7*). [d] Extrapolations of the pertinent property values according to equation analogous to Eq. (*8*).

TABLE VII

Sensitivity of mean electric properties of cyanoborane isomers (in a.u.) to geometry changes. Properties were evaluated at the MP2/aug-cc-pVDZ level. Geometries have been obtained with the methods and basis sets indicated in the header of the Table. Numbers in parentheses are the deviations (in %) from the values obtained in the CCSD(T)/cc-pVTZ geometry

Method	MP2 (frozen core)	MP2 (frozen core)	MP2 (frozen core)	MP2 (frozen core)	DFT-B3LYP	CCSD(T)
Basis set	DZP (Dunning)	cc-pVTZ	aug-cc-pVDZ	aug-cc-pVTZ	DZP (Dunning)	cc-pVTZ
H_2BCN						
μ	1.1231	1.1081	1.1223	1.1102	1.0966	1.0990
	(2.2)	(0.8)	(2.1)	(1.0)	(–0.2)	
$\bar{\alpha}^a$	30.103	29.755	30.350	29.768	29.883	29.757
	(1.2)	(0.0)	(2.0)	(0.0)	(0.4)	
$\beta_{\|\|}$	–59.3	–58.2	–60.1	–58.4	–56.4	–56.2
	(5.5)	(3.6)	(6.9)	(3.9)	(0.4)	
$\gamma_{\|\|}$	3911	3802	3963	3805	3832	3800
	(2.9)	(0.1)	(4.3)	(0.1)	(0.8)	
HCNBH (open form)						
μ	1.1538	1.1425	1.1446	1.1395	1.1392	1.1392
	(1.3)	(0.3)	(0.5)	(0.0)	(0.0)	
$\bar{\alpha}$	40.887	40.751	41.102	40.841	41.342	40.592
	(0.7)	(0.4)	(1.3)	(0.6)	(1.8)	
$\beta_{\|\|}$	–89.6	–97.9	–91.3	–101.7	–111.4	–94.6
	(–5.3)	(3.5)	(–3.5)	(7.5)	(17.8)	
$\gamma_{\|\|}$	16429	16984	16449	17180	17850	16938
	(–3.0)	(0.3)	(–2.9)	(1.4)	(5.4)	
HCNBH (cyclic form)						
μ	0.7136	0.7081	0.7112	0.7080	0.6991	0.7071
	(0.9)	(0.1)	(0.6)	(0.1)	(–1.1)	
$\bar{\alpha}$	29.158	28.843	29.468	28.877	29.170	28.920
	(0.8)	(–0.3)	(1.9)	(–0.1)	(0.9)	
$\beta_{\|\|}$	–23.0	–22.7	–24.5	–23.1	–25.3	–23.1
	(–0.4)	(–1.7)	(6.1)	(0.0)	(9.5)	
$\gamma_{\|\|}$	4798	4733	4891	4758	4880	4764
	(0.7)	(–0.7)	(2.7)	(–0.1)	(2.4)	

[a] The mean polarizability $\bar{\alpha}$ is defined as $\bar{\alpha} = 1/3 \sum_{\xi} \alpha_{\xi\xi}$.

tions using different optimised geometries. The averaged values are shown in Table VII. Some facts are worth noting. (i) Closeness of the cc-pVTZ and aug-cc-pVTZ geometry parameters obtained at the same correlated level (see Tables I–III) is naturally reflected in the conformity of the corresponding electric properties. This also supports the use of CCSD(T)/cc-pVTZ in the forthcoming calculations for monomers. (ii) As expected from comparison of structural parameters, the use of MP2/DZP and MP2/aug-cc-pVDZ geometries should possibly be avoided, though the property values are still qualitatively accurate. (iii) The use of DFT-B3LYP/DZP geometry has been found appropriate merely for H_2BCN; in spite of apparent accuracy of the structural parameters for HCNBH (both open and cyclic forms), larger discrepancies appear in respective properties (particularly β). (iv) On the contrary, the property values calculated in the MP2/cc-pVTZ and CCSD(T)/cc-pVTZ geometries are very close to each other for all the investigated systems. As a good compromise between the accuracy and computational demands, e.g. for the future investigation of the electronic component of electric properties of cyanoborane oligomers, we therefore recommend the use of geometries optimized at the MP2/cc-pVTZ level. This is in accord with the conclusion made by Reis et al. for acetonitrile[88].

Electron Correlation Effects

Electron correlation effects on electric properties of the systems investigated by means of MP2, CCSD (with relaxed as well as unrelaxed MO orbitals) and CCSD(T) are shown in Table VIII. These results have been obtained for CCSD(T)/cc-pVTZ geometries using the aug-cc-pVDZ basis set. Let us underline that freezing of the core orbitals has only a minor effect on calculated properties and thus in our discussion we do not have to distinguish between the results obtained with and without the core interaction.

As expected, for the systems with multiple bonds, inclusion of the electron correlation effects in evaluation of electric properties is essential. Indeed, the electron correlation effects estimated from the difference between the CCSD(T) and RHF values bring a significant decrease (by 10–20%) of dipole moments, increase of dipole polarizabilities by 3–7%, and a dramatic increase (25–30%) in the second hyperpolarizabilities. Though the electron correlation contribution to the parallel first hyperpolarizability is less systematic, its importance is evident.

When searching for a relatively cheap correlation method we are naturally interested in performance of the MP2. It can be seen that MP2 tends to overestimate the CCSD(T) dipole moments of our systems by 2–5%, with

TABLE VIII
Electric properties of cyanoborane isomers (in a.u.) calculated in the CCSD(T)/cc-pVTZ geometry using aug-cc-pVDZ basis set and various correlated methods. Values calculated with the frozen core orbitals are in italics

Property	RHF	MP2	CCSD	CCSD (unrelaxed MO)	CCSD(T)
H_2BCN					
μ	1.2360	1.0988	1.1114	1.1114	
		1.0990	*1.1113*	*1.1113*	*1.0812*
$\bar{\alpha}$	29.390	29.754	29.850	30.135	
		29.757	*29.857*	*30.127*	*30.135*
$\beta_{\|\|}$	–64.8	–56.2	–61.6	–68.7	
		–56.2	*–61.7*	*–68.7*	*–68.7*
$\gamma_{\|\|}$	3093	3797	3831	4176	
		3800	*3840*	*4179*	*4161*
HCNBH (open form)					
μ	1.3171	1.1377	1.1211	1.1211	
		1.1392	*1.1218*	*1.1218*	*1.0802*
$\bar{\alpha}$	37.323	40.586	39.619	40.673	
		40.592	*39.625*	*40.673*	*40.307*
$\beta_{\|\|}$	–115.6	–94.6	–81.3	–113.2	
		–94.4	*–81.3*	*–113.7*	*–92.9*
$\gamma_{\|\|}$	12376	16910	14784	16468	
		16938	*14811*	*16499*	*16210*
HCNBH (cyclic form)					
μ	0.7630	0.7070	0.7005	0.7005	
		0.7071	*0.7003*	*0.7003*	*0.6844*
$\bar{\alpha}$	27.942	28.914	28.728	29.197	
		28.920	*28.739*	*29.196*	*29.032*
$\beta_{\|\|}$	–25.0	–23.1	–25.5	–30.5	
		–23.1	*–25.7*	*–30.6*	*–27.6*
$\gamma_{\|\|}$	3284	4758	4431	4976	
		4764	*4409*	*4986*	*4779*

the largest error being 0.06 a.u. for the open form HCNBH. MP2 mean dipole polarizabilities differ from those obtained at the CCSD(T) level by less than 2%. The largest discrepancies between MP2 and CCSD(T) can be observed in the case of parallel first hyperpolarizabilities, where the deviations from the CCSD(T) values reach 15–20% for borazirene and H_2BCN. For the open form of HCNBH with the largest $\beta_{||}$ the MP2 – CCSD(T) difference of 2% is more than acceptable. For the mean second hyperpolarizabilities, the MP2 method provides values whose deviations from CCSD(T) are within 10%. Like for $\beta_{||}$, the largest $\gamma_{||}$ is predicted for the open form of HCNBH. For this molecule the difference between the MP2 and CCSD(T) values is about 700 a.u., i.e. 4% of the latter.

As the two CCSD columns in the pertinent tables show, the orbital relaxation effect can be quite large especially for higher-order properties. In some cases (e.g. H_2BCN), the absence of orbital relaxation in CCSD has brought about the same effect as inclusion of triple excitations in CCSD(T), which leads to a very good agreement between the two approaches. Similar behavior has been found previously[46,47,88]. To be pragmatic, if one does not go to CCSD(T) within the "relaxed-orbital" approach, the use of MP2 with the aforementioned relatively small basis sets is more reliable.

Frequency-Dependent Properties of H_2BCN

The frequency-dependent (hyper)polarizabilities of H_2BCN calculated using the CCSD response theory with the aug-cc-pVDZ and aug-cc-pVTZ basis sets in the CCSD(T)/cc-pVTZ geometry are presented in Tables IX–XI. The tables also contain extrapolated values obtained from aug-cc-pVDZ and aug-cc-pVTZ values by the CBS-B2 scheme described in Section Basis Sets. On the basis of results for static properties we estimate uncertainties of the frequency-dependent CBS-B2 α to be about 0.1% and errors of the aug-cc-pVTZ β and γ values within about 2%.

From Table IX it can be seen that the differences between the aug-cc-pVDZ and aug-cc-pVTZ mean polarizability values do not practically depend on the frequency within the investigated region of the spectrum. The estimated averaged and anisotropic electronic polarizabilities at ∞, 694.3 and 632.8 nm wavelengths obtained from the CBS-B2 values can be respectively represented by the fit (in a.u.)

$$\overline{\alpha}(\omega) \approx 30.177(1 + 4.500\,\omega^2 + 34.723\omega^4) \qquad (9)$$

and

$$\Delta\alpha(\omega) \approx 18.323(1 + 8.337\omega^2 + 89.308\,\omega^4)\,. \qquad (10)$$

In the low-frequency region of the spectrum, the dispersion of the dc-Pockels and SHG responses can be respectively described by the fourth-order fit (in a.u.) using the aug-cc-pVTZ values as follows:

$$\beta_{||}^{\text{dc-Pockels}}(\omega) \approx -62.00\left(1 + 6.73\omega_L^2 + 45.25\omega_L^4\right) \qquad (11)$$

and

$$\beta_{||}^{\text{SHG}}(\omega) \approx -62.00\left(1 + 1.84\omega_L^2 + 8.40\,\omega_L^4\right) \qquad (12)$$

where $\omega_L^2 = 2\omega^2$ for the dc-Pockels effect and $\omega_L^2 = 6\omega^2$ for the SHG response (see refs[12,90] and references therein for discussion of various expansions in frequency). The use of the fourth-order fit is supported by work of Hättig[91] who has extended the dispersion relations through eighth-order in ω and has shown that a single fourth-order coefficient suffices to describe first hyperpolarizabilities as well as second hyperpolarizabilities with one or more static fields. Based on the latter we can describe the frequency disper-

TABLE IX
Static and dynamic polarizabilities (in a.u.) of H_2BCN calculated using the CCSD response theory with aug-cc-pVDZ and aug-cc-pVTZ basis sets in CCSD(T)/cc-pVTZ geometry. Inner-shell orbitals were kept frozen

Basis set	λ, nm	α_{xx}	α_{yy}	α_{zz}	$\bar{\alpha}$	$\Delta\alpha$
aug-cc-pVDZ	∞	25.376	22.229	42.777	30.127	19.169
aug-cc-pVTZ	∞	25.455	22.488	42.517	30.153	18.723
CBS-B2[a]	∞	25.525	22.721	42.284	30.177	18.323
aug-cc-pVDZ	694.3	25.755	22.577	43.874	30.735	19.899
aug-cc-pVTZ	694.3	25.836	22.845	43.598	30.759	19.431
CBS-B2[a]	694.3	25.909	23.084	43.349	30.781	19.011
aug-cc-pVDZ	632.8	25.834	22.651	44.108	30.864	20.056
aug-cc-pVTZ	632.8	25.916	22.920	43.828	30.888	19.583
CBS-B2[a]	632.8	25.989	23.161	43.576	30.909	19.159

[a] Extrapolations of the pertinent property values according to equation analogous to Eq. (*8*).

sion of the dc-Kerr response within the region of ∞, 694.3 and 632.8 nm wavelengths by the fit (in a.u.) through the aug-cc-pVTZ values as follows:

$$\gamma_{||}^{\text{dc-Kerr}}(\omega) \approx 4442\left(1 + 4.94\omega_{\mathrm{L}}^{2} + 25.98\,\omega_{\mathrm{L}}^{4}\right) \qquad (13)$$

where $\omega_{\mathrm{L}}^{2} = 2\omega^{2}$.

TABLE X
Static and dynamic first hyperpolarizabilities (in a.u.) of H_2BCN calculated using the CCSD response theory with aug-cc-pVDZ and aug-cc-pVTZ basis sets in CCSD(T)/cc-pVTZ geometry. Inner-shell orbitals were kept frozen

Basis set	λ, nm	β_{xxz}	β_{zxx}	β_{yyz}	β_{zyy}	β_{zzz}	$\beta_{\|\|}$
aug-cc-pVDZ	∞	–19.60	–19.60	–7.95	–7.95	–87.01	–68.73
aug-cc-pVTZ	∞	–14.09	–14.09	–4.83	–4.83	–84.41	–62.00
CBS-B2[a]	∞	–9.15	–9.15	–2.03	–2.03	–82.09	–55.96
aug-cc-pVDZ	dc-Pockels:694.3	–20.51	–20.75	–8.41	–8.94	–99.17	–77.16
aug-cc-pVTZ	dc-Pockels:694.3	–14.90	–15.02	–5.27	–5.68	–96.18	–70.02
CBS-B2[a]	dc-Pockels:694.3	–9.87	–9.88	–2.45	–2.76	–93.50	–63.62
aug-cc-pVDZ	dc-Pockels:632.8	–20.71	–21.00	–8.52	–9.16	–101.97	–79.09
aug-cc-pVTZ	dc-Pockels:632.8	–15.08	–15.22	–5.37	–5.88	–98.89	–71.86
CBS-B2[a]	dc-Pockels:632.8	–10.03	–10.04	–2.55	–2.93	–96.12	–65.38
aug-cc-pVDZ	SHG:694.3	–22.82	–23.88	–10.39	–12.68	–133.21	–100.52
aug-cc-pVTZ	SHG:694.3	–16.87	–17.46	–7.06	–8.89	–129.02	–92.26
CBS-B2[a]	SHG:694.3	–11.54	–11.70	–4.09	–5.50	–125.25	–84.84
aug-cc-pVDZ	SHG:632.8	–23.58	–25.01	–11.20	–14.23	–147.46	–110.23
aug-cc-pVTZ	SHG:632.8	–17.54	–18.35	–7.82	–10.25	–142.72	–101.50
CBS-B2[a]	SHG:632.8	–12.12	–12.39	–4.79	–6.67	–138.48	–93.66
aug-cc-pVDZ	OR:694.3	–20.75	–20.51	–8.94	–8.41	–99.17	–77.16
aug-cc-pVTZ	OR:694.3	–15.02	–14.90	–5.68	–5.27	–96.18	–70.02
CBS-B2[a]	OR:694.3	–9.88	–9.87	–2.76	–2.45	–93.50	–63.62
aug-cc-pVDZ	OR:632.8	–21.00	–20.71	–9.16	–8.52	–101.97	–79.09
aug-cc-pVTZ	OR:632.8	–15.22	–15.08	–5.88	–5.37	–98.89	–71.86
CBS-B2[a]	OR:632.8	–10.04	–10.03	–2.93	–2.55	–96.12	–65.38

[a] Extrapolations of the pertinent property values according to equation analogous to Eq. (*8*).

TABLE XI
Static and dynamic first hyperpolarizabilities (in a.u.) of H_2BCN calculated using the CCSD response theory with aug-cc-pVDZ and aug-cc-pVTZ basis sets in CCSD(T)/cc-pVTZ geometry. Inner-shell orbitals were kept frozen.

NLO process Basic set	γ_{xxxx}	γ_{yyyy}	γ_{zzzz}	γ_{xxyy}	γ_{xyyx}	γ_{yxxy}	γ_{yyzz}	γ_{yzzy}	γ_{zyyz}	γ_{xxzz}	γ_{xzzx}	γ_{zxxz}	$\gamma_{\|\|}$
Static limit													
aug-cc-pVDZ	2819	2169	9392	673	673	673	1123	1123	1123	1463	1463	1463	4179
aug-cc-pVTZ	3156	2417	9375	854	854	854	1252	1252	1252	1525	1525	1525	4442
CBS-B2[a]	3458	2640	9360	1017	1017	1017	1369	1369	1369	1580	1580	1580	4677
dc-Kerr: 694.3 nm													
aug-cc-pVDZ	3018	2329	10492	721	718	721	1247	1211	1237	1588	1554	1591	4585
aug-cc-pVTZ	3369	2588	10452	915	907	911	1380	1346	1374	1649	1620	1657	4855
CBS-B2[a]	3683	2821	10416	1089	1077	1082	1499	1467	1498	1705	1679	1716	5097
dc-Kerr: 632.8 nm													
aug-cc-pVDZ	3062	2364	10744	732	727	732	1275	1232	1262	1615	1574	1619	4676
aug-cc-pVTZ	3414	2625	10698	928	919	924	1409	1368	1402	1677	1641	1686	4947
CBS-B2[a]	3731	2860	10657	1105	1090	1096	1528	1489	1527	1732	1701	1746	5190
THG: 694.3 nm													
aug-cc-pVDZ	4402	3604	22742	1041	1041	1157	2540	2540	2631	2334	2334	2679	8626
aug-cc-pVTZ	4819	3919	22329	1305	1305	1424	2643	2643	2765	2397	2397	2737	8868
CBS-B2[a]	5194	4202	21958	1542	1542	1663	2735	2735	2884	2453	2453	2788	9084
THG: 632.8 nm													
aug-cc-pVDZ	4884	4380	31773	1152	1152	1526	4188	4188	3639	2607	2607	3187	11467
aug-cc-pVTZ	5315	4668	31071	1440	1440	1804	4117	4117	3738	2666	2666	3232	11610
CBS-B2[a]	5703	4926	30441	1699	1699	2054	4054	4054	3828	2719	2719	3272	11739
DFWM: 694.3 nm													
aug-cc-pVDZ	3241	2511	11912	774	782	782	1340	1468	1468	1695	1770	1770	5085
aug-cc-pVTZ	3604	2782	11837	973	998	998	1483	1593	1593	1765	1821	1821	5339
CBS-B2[a]	3931	3025	11770	1152	1191	1191	1611	1706	1706	1828	1867	1867	5605
DFWM: 632.8 nm													
aug-cc-pVDZ	3338	2592	12606	801	808	808	1395	1564	1564	1750	1845	1845	5322
aug-cc-pVTZ	3708	2868	12513	1004	1031	1031	1540	1687	1687	1822	1894	1894	5597
CBS-B2[a]	4039	3115	12429	1186	1232	1232	1671	1797	1797	1886	1937	1937	5843

[a] Extrapolations of the pertinent property values according to equation analogous to Eq. (*8*).

CONCLUSIONS

Dipole moments, polarizabilities and first and second hyperpolarizabilities of three selected cyanoborane isomers have been calculated using various quantum chemistry methods including RHF, MP2, CCSD and CCSD(T). Dependences of their electric properties on the quality of the basis set, sensitivity of the properties to the accuracy of molecular structural parameters, electron correlation effects and the frequency dispersion of the properties of the most stable isomer have been investigated.

The largest static electronic nonlinear responses occur for the open form of HCNBH, whose μ, $\bar{\alpha}$, $\beta_{||}$ and $\gamma_{||}$ calculated at the CCSD(T)/ aug-cc-pVDZ level using the CCSD(T)/cc-pVTZ geometry are 1.0802, 40.3071, –92.9 and 16210 a.u., respectively. Conservative error estimates of these values determined from CBS extrapolations and/or reference MP2-R12 calculations are 2% for μ and $\bar{\alpha}$ and about 10% for hyperpolarizabilities. The reliability of cc-pVTZ-optimized geometries is supported by the closeness of the electric properties obtained in MP2/cc-pVTZ and MP2/aug-cc-pVTZ geometries.

On the basis of our study we recommend the following strategy for calculations of electric properties of large systems with similar nature of chemical bonds, such as various isomers of cyanoborane oligo- and polymers.

1. Though the molecular structures should preferably be optimized at the MP2 level using the cc-pVTZ basis set, acceptable results for the electronic components of electric properties can also be obtained with the DFT-B3LYP/DZP geometries.

2. For evaluation of the electronic part of electric properties within the given geometry aug-cc-pVDZ represents a minimum basis set (at least for small oligomers) required to obtain qualitatively correct estimations (i.e. the estimated error bars are 2% for μ and $\bar{\alpha}$, and 10% for $\beta_{||}$ and $\gamma_{||}$).

3. MP2 appears to be a good compromise between the computational demands and the accuracy of results, though it systematically overestimates the CCSD(T) dipole moment values by 2–5%. The deviations for $\bar{\alpha}$ and $\gamma_{||}$ are 2 and 10%, respectively. Parallel first hyperpolarizabilities might be less accurate. Freezing of the core orbitals has only a minor effect on the electric properties.

4. Both extrapolated field-dependent energy derivatives and direct extrapolations of the properties, particularly within Zahradník's CBS-B approach, give very similar results. For dipole moments and polarizabilities both CBS-A and CBS-B schemes using the aug-cc-pV*X*Z (*X* = D, T and *X* = T, Q) basis sets lead to results within 1% error from the reference values. With increasing order of the response property, the accuracy of the extrapolations deteriorates, though for β it remains within about 2% for the CBS-B (X = T, Q) scheme.

5. To achieve similarly accurate estimations of the frequency-dependent properties using the CBS-B2 extrapolation scheme, this scheme can be recommended only up to α, whereas for β and γ it is preferred to use the aug-cc-pVTZ instead of tested extrapolations.

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