Polarizabilities of Carbon Dioxide and Carbodiimide. Assessment of Theoretical Model Dependencies on Dipole Polarizabilities and Dipole Polarizability Anisotropies†

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Received: August 10, 2000; In Final Form: September 19, 2000

The atomic polarizabilities of carbon dioxide and carbodiimide, HN═C═NH, have been studied with ab initio theoretical methods. Structures were optimized and properties were determined using RHF, MP2, and QCISD theories and a variety of basis sets up to quadruple-ζ quality. The static electric dipole polarizability tensor components were determined using the finite field method. The isotropic polarizability $\langle\alpha\rangle$ and the anisotropic polarizabilities $\Delta\alpha$ and κ were calculated for both heterocumulenes from the respective tensor components. The experimental tensor components and polarizabilities $\langle\alpha\rangle$, $\Delta\alpha$, and κ are known for carbon dioxide, and these values are used to assess the accuracy of the theoretical methods. This knowledge about the achievable accuracy is then employed in the prediction of the polarizability values of carbodiimide. The only measurable polarizability values for carbodiimide are $\langle\alpha\rangle$ and κ. The best level of theory employed in this study is QCISD(fc)/6-311++G(3df,2pd) and this level gives $\langle\alpha\rangle$ and κ values of 16.722 and 0.289 au^3 for carbon dioxide. These values deviate somewhat from the experimental values of 17.762 and 0.267 au^3 and we rationalize these differences based on the calculated polarizability tensor components. The calculated $\langle\alpha\rangle$ and κ values of carbodiimide are 28.963 and 0.310 au^3. Taking into account the deviations from experiment for the carbon dioxide values, we predict $\langle\alpha\rangle$ and κ values of 30.764 and 0.286 au^3 for carbodiimide. The discussion emphasizes the important role of the inclusion of three sets of d-polarization functions. The third, diffuse set of d-functions is essential to polarize the electron density described by the diffuse functions and also by the outer valence p-functions.

Introduction

Over the past 40 years the chemistry of carbodiimides has proliferated from reagents for peptide and nucleotide syntheses[1,2] to include many important roles in a wide array of chemical applications.[3] Carbodiimides are used in the formation of heterocycles via cycloaddition reactions, they have broad utility in biochemical processes, and they are important in polymer chemistry.[3] The most important reactions of carbodiimides all involve nucleophilic attack across one of the imine bonds and the nucleophilic addition of water to dicyclohexylcarbodiimide is widely used for dehydration.[4] We are particularly interested in the hydrolysis and acidolysis of carbodiimides for their potential role as reactive intermediates in guanine deamination.[5−8] We proposed a mechanism to account for the presence of oxanosine in the deamination of guanine.[6] Our mechanism suggests that one route for the dediazoniation of guanine involves a pyrimidine ring opening by N1−C6 bond cleavage resulting in an imidazole derivative with a carbodiimide group at the 4-position and a carboxylic acid at the 5-position. The chemistry of this intermediate then involves nucleophilic additions (of water and carboxylic acid) to the carbodiimide.[6]

In spite of the widespread interest in carbodiimides, there have been surprisingly few mechanistic studies of its addition chemistry. There have been a few experimental studies of the addition of carboxylic acids to dicyclohexylcarbodiimide,[9] but, to our knowledge, there have not been any studies of the addition of water to carbodiimide. An even more astonishing fact is that the subject has been overlooked by theoreticians. Computational studies were performed on the parent carbodiimide, HN═C═NH, but they focused on the geometry and spectroscopic properties of the equilibrium structure,[10,11] the electronics of the *N*-inversion,[12] and the torsional−rotational dynamics.[13] Therefore, we began ab initio molecular orbital studies of the kinetics of the hydrolysis and acidolysis of the parent carbodiimide and related heterocumulenes. A Communication on the hydrolysis of carbodiimide has recently been published.[14] We have also investigated the charge distributions of heterocumulenes, and we have reported studies of the quadrupole moments of carbon dioxide[15] and carbodiimide.[16] Current research aims at constructing the connection between the properties of the precoordination complexes and the electrical moments of the substrates to further our understanding of the hydrolyses of carbodiimide[14] and carbon dioxide.[17]

In the first step of nucleophilic addition, carbodiimides and carbon dioxide form rather strong van der Waals complexes with nucleophiles. The bonding in these complexes is largely electrostatic with contributions due to H-bonding and other dipole−dipole as well as dipole−quadrupole interactions. To better understand the electrostatic bonding in these complexes, one needs to learn about the charge distribution and the electrostatic moments of the heterocumulenes. The dipole and quadrupole moments are two pertinent properties in this context, and we have studied both of these properties for carbon dioxide[15] and carbodiimide[16] in some detail.[18] In this study we probe deeper into the charge distribution of these molecules via a higher level ab initio quantum-mechanical study of the electric dipole polarizabilities of $C(NH)_2$ and CO_2. Instead of just hoping

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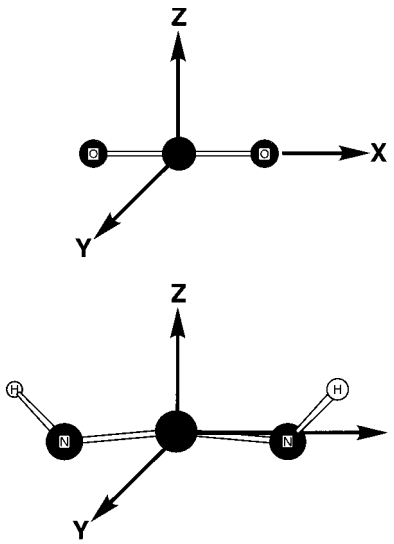
† Part 4 in the series "Nucleophilic Additions to Heterocumulenes." For parts 1−3, see refs 14−16.

10.1021/jp002927r CCC: $19.00
Published on Web 11/10/2000

SCHEME 1: Orientation of Carbon Dioxide and Carbodiimide



for convergence at the best levels employed, we are providing a direct comparison to the experimentally determined electric dipole polarizabilities of carbon dioxide. In addition, the discussion provides conceptual insights as to the relation between the electron density distribution and the quadrupole moment tensor components. In particular, we provide an explanation as to why three sets of d-type polarization functions are required for the accurate reproduction of the polarizabilities of carbon dioxide and of carbodiimide.

Theoretical Methods and Computations

Electrical Dipole Polarizability Tensor Components. The static polarizability tensor components α_{ij} were determined using the finite field method[19] with an electric field step size of 0.001 89 atomic units. We chose the orientation of carbon dioxide and carbodiimide as depicted in Scheme 1. For carbon dioxide the C and O atoms all lie in the *xz*-plane and the C═O bonds are collinear with the *x*-axis. Carbodiimide is positioned in a similar fashion with its C_2 axis aligned with the *z*-axis. The reduced symmetry of carbodiimide precludes the C═NH bond from lying on the *x*-axis. None of the computed polarizability tensor elements of carbon dioxide or carbodiimide is *exactly* zero but many are *very close* to zero. For carbon dioxide, we report only the diagonal elements α_{xx} and $\alpha_{yy} = \alpha_{zz}$. With the selected orientation, α_{xx} is $\alpha_{||}$ and $\alpha_{yy} = \alpha_{zz}$ are $\alpha_{\perp}$. For carbodiimide, we report the three diagonal elements α_{ii} and α_{xy}; the elements α_{xz} and α_{yz} are near-zero.

The average optical polarizability α of a dilute gas with number density N can be determined by measurement of the refractive index n, $\langle\alpha\rangle = (n - 1)/(2\pi N)$. This average or isotropic polarizability $\langle\alpha\rangle$ is related to the diagonal elements of the polarizability tensor via

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

Polarizability anisotropies can be determined from measurement of scattering depolarization ratios (Strutt effect) and from refractive index anisotropies (Kerr effect). Light scattering theory describes polarizability anisotropy by κ^2 and this value is related to the polarizability tensor by way of the following equation

$$\kappa^2 = [(\alpha_{11} - \alpha)^2 + (\alpha_{22} - \alpha)^2 + (\alpha_{33} - \alpha)^2]/6\alpha^2$$

In the special case of a linear molecule, two of the diagonal elements are identical, $\alpha_{\perp} = \alpha_{yy} = \alpha_{zz}$, and the polarization anisotropy becomes

$$\kappa = (\alpha_{||} - \alpha_{\perp})/3\alpha$$

We will be computing the value of κ for carbon dioxide and for carbodiimide. The value of κ provides a *relative* measure of anisotropy and this value is relative to the isotropic polarizability. For a comparison of polarization anisotropy in *absolute* terms, the polarizability anisotropy $\Delta\alpha$ can be used and it is defined by

$$\Delta\alpha = \alpha_{||} - \alpha_{\perp}$$

This absolute polarizability anisotropy $\Delta\alpha$ can be and has been measured for carbon dioxide (vide infra). For carbodiimide, no such relation exists for $\Delta\alpha$. Yet, it is instructive to use a similarly defined quantity

$$\Delta\alpha' = \alpha_{xx} - 0.5(\alpha_{yy} + \alpha_{zz})$$

as an index of the carbodiimide's "absolute polarizability anisotropy".

Several units are in use for polarizabilities. Most frequently, polarizabilities are given in units of $Å^3$ or $C^2\ m^2\ J^{-1}$. The conversion is accomplished by $Å^3 = 10^{-30}\ C^2\ m^2\ J^{-1}$. We compute the polarizabilities in atomic units (1 au = 0.529 177 Å) and polarizabilities given in $Å^3$ need to be divided by 0.148 185 to obtain the numbers in au^3.

Description of ab Initio Theoretical Levels. The determination of the desired properties requires the electron density distribution $\rho(\mathbf{r})$ for a given nuclear configuration and we determined $\rho(\mathbf{r})$ using restricted Hartree−Fock theory, Møller−Plesset perturbation theory, MP2(full), and quadratic configuration interaction theory, QCISD(fc).[20,21] Several basis sets were employed in conjunction with these three methods. The smallest of these basis sets were the 6-31G* and 6-31G** basis sets.[22] The next two basis sets employed are 6-311G** and 6-311++G**.[23,24] The step from a double-ζ to a triple-ζ valence description is a major improvement. Further improvement is achieved by additional flexibility in the number and the type of the polarization functions and we considered three options:[25] 6-311G(2d,p), 6-311G(2df,p), and 6-311G(3df,2pd). Finally, all of these basis sets also were employed with augmentation by diffuse functions. The valence double-ζ basis set D95V(d,p)[26] and some of Dunning's correlation-consistent basis sets cc-pV*n*Z[27] also were employed. The cc-pVTZ basis sets is comparable to the 6-311G(2df,p) basis set in terms of basis functions, but the former features a much larger number of primitives. These basis sets again were also used with augmentation by diffuse functions (with the exponents used in the Pople basis sets). Note that this procedure differs from the usual diffuse function augmentation of the cc-pV*n*Z type basis sets which adds one diffuse function of each function type (including d- and f-functions).

We optimized all structures with each of the three theoretical methods and with each of the basis sets. The ab initio calculations were carried out with the program Gaussian94[28] on a Silicon Graphics PowerChallenge L minisupercomputer. We previously reported the total energies, optimized structures, atomic charges, and vibrational frequencies for both carbon dioxide[15] and carbodiimide[16] and thus we will focus on the selected electric dipole polarizability data collected in Tables 1 and 2. Extended versions of Tables 1 and 2 with all the data

TABLE 1: Electrical Dipole Polarizability Parameters for Carbon Dioxide[a]

theoretical level	$\alpha_{\|}$[b]	$\alpha_{\perp}$[c]	$\langle\alpha\rangle$	κ	$\Delta\alpha$
MP2(full)-theory					
6-311G(2d)	24.081	9.582	14.415	0.335	14.499
6-311+G(2d)	27.602	10.568	16.246	0.349	17.034
6-311G(2df)	23.647	9.547	14.247	0.330	14.100
6-311+G(2df)	27.305	10.530	16.121	0.347	16.775
6-311G(3d)	24.873	11.372	15.872	0.284	13.502
6-311+G(3d)	27.897	12.242	17.461	0.299	15.655
6-311G(3df)	24.651	11.361	15.791	0.281	13.290
6-311+G(3df)	27.578	12.178	17.311	0.297	15.400
cc-pVTZ	25.181	9.910	15.000	0.339	15.271
cc-pVTZ+	26.495	10.246	15.662	0.346	16.250
QCISD(fc)-theory					
6-311G(2d)	23.168	9.415	13.999	0.327	13.753
6-311+G(2d)	26.452	10.329	15.703	0.342	16.123
6-311G(2df)	22.993	9.417	13.942	0.325	13.576
6-311+G(2df)	27.305	10.530	16.121	0.347	16.775
6-311G(3d)	23.986	11.174	15.445	0.277	12.812
6-311+G(3d)	26.801	11.970	16.914	0.292	14.831
6-311G(3df)	23.724	11.147	15.340	0.273	12.577
6-311+G(3df)	26.402	11.883	16.722	0.289	14.519
cc-pVTZ	24.181	9.715	14.537	0.332	14.466
cc-pVTZ+	25.386	10.023	15.144	0.338	15.363
exptl values[29]	27.250	13.018	17.762	0.267	14.232
percentage *m*[d]	3.21	9.55	6.22	−7.61	−1.98

[a] All values in au^3. [b] $\alpha_{\|} = \alpha_{xx}$. [c] $\alpha_{\perp} = \alpha_{yy} = \alpha_{zz}$. [d] $m = -100$(6-311+G(3df)-value − exptl value)/6-311+G(3df)-value.

determined at all theoretical levels can be found in the Supporting Information. The data for carbodiimide are illustrated in Figures 1 and 3. Similar figures for carbon dioxide are contained in the Supporting Information.

Results and Discussion

Experimental Data. The experimentally determined values for the electric dipole polarizability of carbon dioxide are given in Table 1: $\alpha_{xx} = 27.250$ au^3 and $\alpha_{yy} = \alpha_{zz} = 13.018$ au^3.[29] The electric dipole polarizabilities $\langle\alpha\rangle$, κ, and $\Delta\alpha$ of carbon dioxide are 17.762, 0.267, and 14.232 au^3, respectively.[29] The polarizability of carbon dioxide has been the topic of several previous high-level theoretical studies.[30] The atomic polarizabilities of C, O, N, and H are important when discussing the effects of bonding on polarizability and they are given in Table 3. The measured polarizabilities of O and N are 7.6 and 5.2 au^3, respectively.[31] The atomic polarizability of C was calculated by Das and Thakkar using the CCSD(T) method in conjunction with a [10s, 7p, 7d, 6f] basis set.[32] This level of theory was shown to reproduce the atomic polarizability values of N and O and it gives a value of 11.7 au^3 for C. The atomic polarizability of H is 4.5 au^3 and this is the exact value obtained from calculation.[33]

Electric Dipole Polarizability Tensor Component α_{xx}. The theoretical level and basis set dependencies of the nonzero electrical dipole polarizability tensor components of carbodiimide are illustrated in Figure 1. The electric dipole polarizability tensor component α_{xx} measures the polarizability along the CO bond in carbon dioxide and in carbodiimide the value approximately measures the polarizability along the CN bond. The calculated electric dipole polarizability tensor component α_{xx} of carbon dioxide is between 19 and 23 au^3 at the RHF level and between 23 and 29 au^3 when electron correlation is considered. The α_{xx} value of carbodiimide is almost *2 times* that of carbon dioxide. The RHF method gives values between 38 and 42 au^3, and the MP2 and QCISD methods increase the value to between 41 and 49 au^3. It is expected that α_{xx} is greater for carbodiimide because of the atomic polarizabilities of N and O. Nitrogen is more polarizable than oxygen[31] (Table 3), and thus we would predict greater polarizability along a CN bond than along a CO bond.

The experimentally measured electric dipole polarizability tensor component α_{xx} of carbon dioxide is 27.25 au^3, and this value is well reproduced at most of the electron-correlated levels when diffuse functions are included in the basis set. An explanation as to why electron correlation is needed to reproduce the experimental results would require electron density difference maps computed with the uncorrelated and correlated methods, and this is an issue we plan to address in the future.

It is important to recognize that α_{xx} is highly sensitive to the presence of diffuse functions in the basis set. The inclusion of

TABLE 2: Electrical Dipole Polarizability Parameters for Carbodiimide[a]

theoretical level	α_{xx}	α_{xy}	α_{yy}	α_{zz}	$\langle\alpha\rangle$	κ	$\Delta\alpha'$
MP2(full)-theory							
6-311G(2d,p)	41.827	−2.197	15.489	15.324	24.213	0.364	26.420
6-311++G(2d,p)	47.893	−1.251	18.420	18.272	28.195	0.349	29.547
6-311G(2df,p)	41.742	−2.090	15.496	15.302	24.180	0.363	26.344
6-311++G(2df,p)	47.590	−1.210	18.277	18.113	27.994	0.350	29.395
6-311G(3d,2pd)	42.897	−2.013	18.294	18.145	26.445	0.311	24.677
6-311++G(3d,2pd)	47.991	−1.349	20.466	20.312	29.590	0.311	27.602
6-311G(3df,2pd)	42.888	−1.999	18.263	18.100	26.417	0.312	24.706
6-311++G(3df,2pd)	47.878	−1.366	20.354	20.190	29.474	0.312	27.605
cc-pVTZ	43.365	−1.865	16.613	16.487	25.488	0.351	26.815
cc-pVTZ++	45.402	−1.705	17.583	17.460	26.815	0.347	27.880
QCISD(fc)-theory							
6-311G(2d,p)	41.525	−2.390	15.572	15.325	24.140	0.360	26.076
6-311++G(2d,p)	47.116	−1.506	18.282	18.069	27.822	0.347	28.941
6-311G(2df,p)	41.357	−2.290	15.569	15.307	24.078	0.359	25.919
6-311++G(2df,p)	46.649	−1.481	18.109	17.887	27.548	0.347	28.652
6-311G(3d,2pd)	42.561	−2.198	18.255	18.036	26.284	0.310	24.416
6-311++G(3d,2pd)	47.243	−1.566	20.222	20.013	29.159	0.310	27.126
6-311G(3df,2pd)	42.448	−2.200	18.214	17.985	26.215	0.310	24.348
6-311++G(3df,2pd)	46.940	−1.608	20.084	19.866	28.963	0.310	26.965
cc-pVTZ	42.955	−2.076	16.666	16.452	25.358	0.347	26.397
cc-pVTZ++	44.855	−1.916	17.526	17.334	26.572	0.344	27.425
best estimate[b]	48.447		22.002	21.763	30.764	0.286	26.431

[a] All values in au^3. [b] As calculated at the highest level, QCISD(fc)/6-311++G(3df,2pd), and taking into account the percentage errors *m* determined for carbon dioxide.

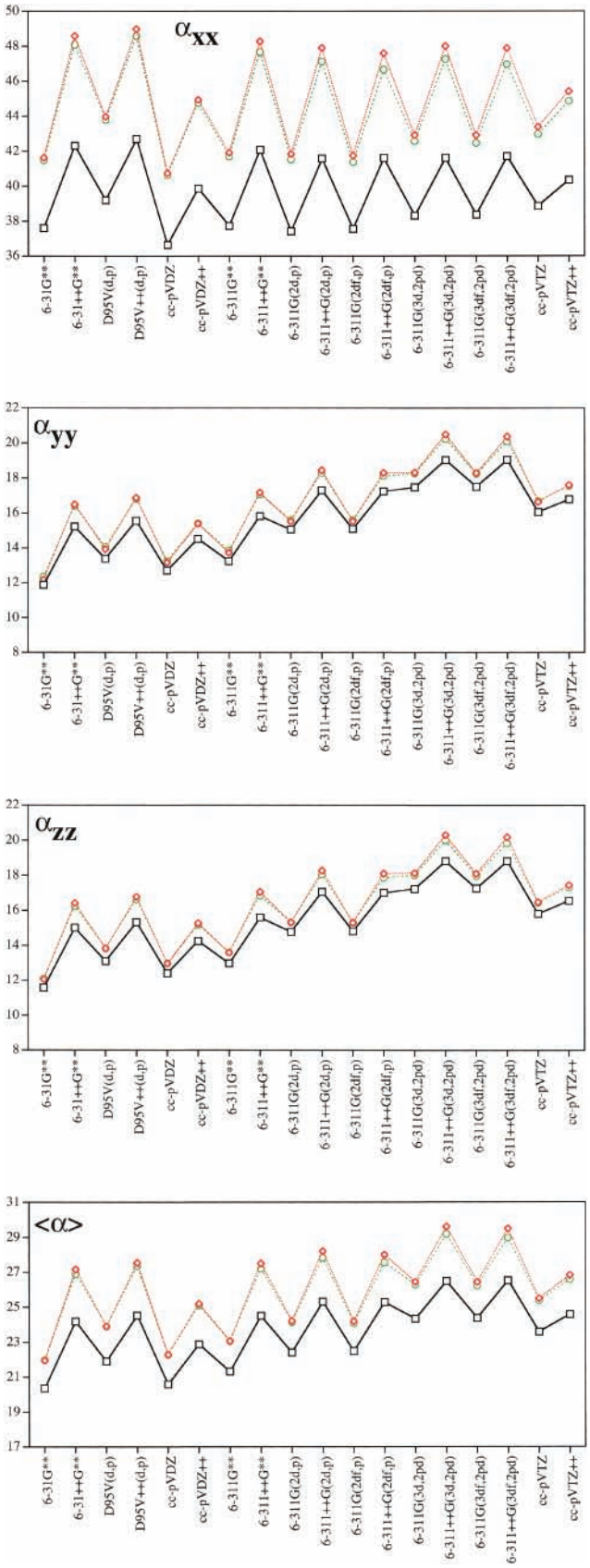


Figure 1. Theoretical level dependency of the atomic polarizability tensor components α_{xx}, α_{yy}, and α_{zz} and the isotropic polarizability $\langle\alpha\rangle$ of carbodiimide. RHF data are marked by squares and connected by solid lines, MP2 data are marked by diamonds and connected by dotted lines, and QCISD data are marked by circles and connected by dashed lines. Units are in au^3.

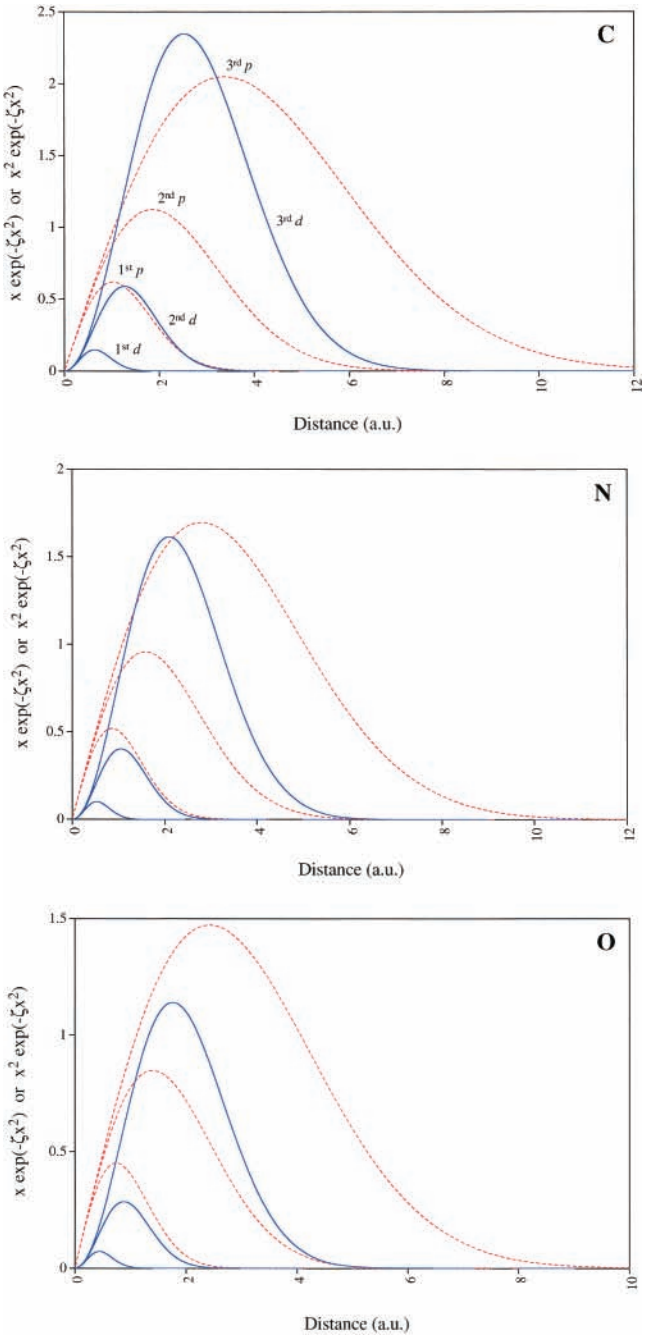


Figure 2. Radial distribution functions $x\exp(-\zeta_i x^2)$ (dashed) and $x^2\exp(-\zeta_i x^2)$ for the p- and d-type primitive functions of C, N, and O (top to bottom). The exponents ζ_i employed are those of the 6-311+G-(3d) basis sets.

diffuse functions increases α_{xx} of carbon dioxide by 2−5 au^3 and that of carbodiimide by 3−7 au^3 (Figure 1a). The α_{xx} value of carbodiimide is more influenced by diffuse functions because nitrogen is more polarizable and its electron density is less contracted than oxygen. It is also significant to note that there is very little difference between the α_{xx} values calculated at the MP2 level and those calculated using the QCISD method. Thus, for larger systems, where the cost of the QCISD method would be prohibitive, we can use the more cost-effective MP2 method.

The experimental α_{xx} value of carbodiimide is not known. Yet, we can make a very accurate prediction of this value with the knowledge of the computed and experimental data for carbon dioxide. We define the values *m* as the percentage deviation between the QCISD/6-311++G(3df,2pd) and the experimental value (bottom of Table 1). Assuming similar errors in the

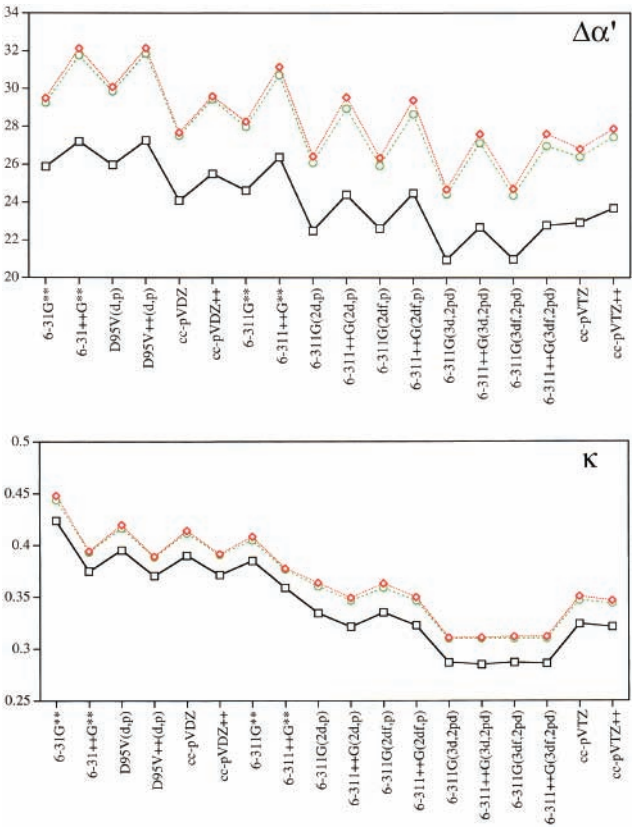


Figure 3. Theoretical level dependency of the polarizability anisotropies $\Delta\alpha$ and κ of carbodiimide. RHF data are marked by squares and connected by solid lines, MP2 data are marked by diamonds and connected by dotted lines, and QCISD data are marked by circles and connected by dashed lines. Units are in au^3.

TABLE 3: Atomic Polarizabilities of Hydrogen, Carbon, Nitrogen, and Oxygen[a]

atom	atomic polarizability	references
H	4.5	33
C	11.7	32
N	7.6	31
O	5.2	3

[a] All values in au^3.

isoelectronic systems should allow for highly accurate predictions of polarizability parameters for carbodiimide by way of α(QCISD/6-311++G(3df,2pd)(1 − *m*/100). Thus, we predict the "best value" for the electric dipole polarizability tensor component α_{xx} value of carbodiimide to be 48.4 au^3. The "best estimates" are collected in the last line in Table 2.

Electric Dipole Polarizability Tensor Components α_{yy} and α_{zz}. The electric dipole polarizability tensor components α_{yy} and α_{zz} of CO_2 and of $C(NH)_2$ measure the polarizability in the direction of the C_2 axis and in the direction perpendicular to the C_2 axis and in the *xy*-plane. For CO_2 these two directions are degenerate and the α_{yy} and α_{zz} values are equal, $\alpha_{yy} = \alpha_{zz} = \alpha_\perp$. The electric dipole polarizability tensor component $\alpha_\perp$ of carbon dioxide is between 7 and 11 au^3 and for carbodiimide the α_{yy} and α_{zz} values are 12−19 au^3. The effect of electron correlation is relatively small for both CO_2 and $C(NH)_2$, increasing the α_{yy} and α_{zz} values by about 1 au^3 with respect to the RHF values (Figure 1, b and c).

As was the case with the α_{xx} value, the α_{yy} and α_{zz} values of CO_2 and $C(NH)_2$ are sensitive to the presence of diffuse functions in the basis set but not as much; the diffuse function augmentation increasing the values by 0.5−2 au^3 for CO_2 and by 1−4 au^3 for $C(NH)_2$. The experimental electric dipole polarizability tensor component $\alpha_\perp$ of carbon dioxide is 13.018 au^3 and, thus, at the best levels of theory α_{yy} remains underestimated by about 1.1 au^3, or 10%. This finding suggests that the π-electron density is not described fully well since $\alpha_\perp$ measures the electric dipole polarizability in the π-planes. The experimental α_{yy} and α_{zz} values of carbodiimide are not known. We can make a prediction based on the value computed with the best theoretical method and accounting for the underestimation via the p-factor. Our "best estimates" for the electric dipole polarizability tensor components α_{yy} and α_{zz} of carbodiimide thus are 22.0 and 21.8 au^3, respectively.

The augmentation of multiple polarization functions affects the $\alpha_{||}$ values and the $\alpha_\perp$ values in significantly different ways. The addition of f-functions has but a small effect in all cases. Large and significant effects are associated with the addition of d-type polarization functions and their effects are much more pronounced for the $\alpha_\perp$ values than for the $\alpha_{||}$ values. Moreover, larger increases of the $\alpha_\perp$ values are observed in going from (2d) → (3d) than in going from (d) → (2d). These systematic basis set effects can be understood by analysis of the exponents of the p- and d-type basis functions summarized in Table 4. In Figure 2, the radial distribution functions are plotted for the p- and d-functions employed in the 6-311+G(3d) basis sets of these atoms. For the p-functions, we consider the three spatially most extended primitives, that is, the two valence function that make up the "11"-part and the single diffuse "+"-function.

The plots in Figure 2 demonstrate in a compelling fashion that there cannot be an adequate polarization of the most diffuse p-functions in the absence of the third set of d-functions. The exponents of polarization functions are determined using some energy parameter, and this process emphasizes polarization effects close to the core. However, for the accurate description of polarizability proper polarization of the outer electron density is required. Note in particular that the first *and the second* sets of d-functions primarily serve to polarize the least diffuse of the three p-functions shown. In other words, the second set of d-functions does not provide polarization of the second-most diffuse set of p-functions (let alone of the most diffuse third set of p-functions).

Isotropic Polarizability $\langle\alpha\rangle$. The calculated isotropic polarizability $\langle\alpha\rangle$ of carbon dioxide is 11−15 au^3 at the RHF level and 13−17 au^3 when electron correlation is considered. Our best values are slightly less than the experimental value of 17.762 au^3 due to the underestimation of the α_{yy} and α_{zz} electric dipole polarizability tensor components. The calculated isotropic polarizability of carbodiimide is almost twice that of carbon dioxide. Again, we would expect this because of the greater atomic polarizability of nitrogen with respect to oxygen. The value of $\langle\alpha\rangle$ of carbodiimide is 20−26 au^3 using the RHF method and 22−29 au^3 using the MP2 or QCISD methods (Figure 1d). The highest level of theory in this study underestimates the $\langle\alpha\rangle$ value of carbon dioxide by approximately 6% and, taking this into account, we would predict an isotropic polarizability $\langle\alpha\rangle$ of carbodiimide of 30.8 au^3.

It is significant to recognize the method and basis set dependencies for the calculation of $\langle\alpha\rangle$ (Figure 1d). Most importantly, the MP2 calculations give the same results as the much more expensive and time-consuming QCISD calculations. The presence of diffuse functions in the basis set is also important in calculating $\langle\alpha\rangle$, and this need stems mostly from the large effect of diffuse functions in calculating the α_{xx} electric dipole polarizability tensor components. Diffuse functions

TABLE 4: Exponents of d-Type Polarization Functions and p-Type Valence and Diffuse Functions on C, N, and O[a]

	first d-coefficient			second d-coefficient			third d-coefficient		
basis set	C	N	O	C	N	O	C	N	O
6-311++G(d,p)	0.626	0.913	1.292						
6-311++G(2df,p)	1.252	1.826	2.584	0.313	0.457	0.646			
6-311++G(3df,2pd)	2.504	3.652	5.168	0.626	0.913	1.292	0.157	0.228	0.323
D95V++(d,p)	0.750	0.800	0.850						
cc-pVDZ++	0.550	0.817	1.185						
cc-pVTZ++	1.097	1.654	2.314	0.318	0.469	0.645			

	first p-coefficient			second p-coefficient			third p-coefficient		
basis set	C	N	O	C	N	O	C	N	O
6-311++G	0.483	0.684	0.906	0.146	0.201	0.256	0.044	0.064	0.085
D95V++	0.359	0.531	0.717	0.115	0.165	0.214	0.044	0.064	0.085
cc-pVDZ++	2.002	2.917	3.854	0.546	0.797	1.046	0.152	0.219	0.275
cc-pVTZ++	1.200	1.742	2.280	0.383	0.555	0.716	0.121	0.173	0.214

[a] The values are given for the three p-primitives with the lowest exponents.

increase the value of $\langle\alpha\rangle$ of carbon dioxide by 1−3 au^3 and of carbodiimide by 2−6 au^3. The value of $\langle\alpha\rangle$ also greatly depends on the number of d-polarization functions for the reasons discussed above (Figure 2).

It is instructive to compare the calculated isotropic polarizability values of CO_2 and $C(NH)_2$ with the sums of the respective atomic polarizabilities of each molecule. It may seem trivial and a common assumption that the sum of the atomic polarizabilities *must* be greater than the molecular isotropic polarizability because the electron density becomes more contracted upon bonding, thus decreasing the overall polarizability. However, a comparison of the molecular isotropic polarizabilities[34] of N_2 and O_2 with the respective atomic polarizabilities of N and O reveals that this issue is not so simple. The molecular isotropic polarizability of N_2 is 11.8 au^3, less than the sum of the atomic polarizabilities of two N atoms ($2\langle\alpha\rangle_N$ = 15.2 au^3) by 3.4 au^3 and in line with the expectation based on the notion of the electron density contracting during bonding. The molecular isotropic polarizability of O_2, however, is 11.0 au^3 and this is *greater* than the sum of the atomic polarizabilities of two O atoms ($2\langle\alpha\rangle_O$ = 10.4 au^3). Thus, it is not a necessity that the molecular isotropic polarizability is less than the sum of the constituent atom's atomic polarizabilities.

The sum of the atomic polarizabilities of one C-atom and two O atoms (Table 3) is 22.1 au^3 and this is 7.0 au^3 greater than our best calculated value for carbon dioxide and 4.3 au^3 greater than the experimental value. For carbodiimide, the sum of the atomic polarizabilities of one C atom, two N atoms, and two H atoms (Table 3) is 35.9 au^3 and this value is about 5 au^3 higher than our computed best estimate of the molecular isotropic polarizability. Thus, both carbon dioxide and carbodiimide are similar to molecular nitrogen in that the sums of their constituent atomic polarizabilities are greater than the molecular isotropic polarizabilities $\langle\alpha\rangle$.

Polarizability Anisotropies Δα. The theoretical level dependencies of the calculated polarizability anisotropies Δα of carbodiimide are displayed in Figure 3. The RHF calculated polarizability anisotropies Δα of carbon dioxide is 10−15 au^3 and electron correlation increases the value to 12.5−20 au^3. Electron correlation increases the value of Δα by 3−5 au^3 with respect to the RHF method and there is little difference between the MP2 and QCISD numbers. The use of three sets of d-functions is critical for the accurate calculation of Δα because of the above-discussed sensitivity of $\alpha_\perp$ to the basis set augmentation with polarization functions (Figure 2).

The polarizability anisotropy of carbodiimide is almost twice as high as the value for carbon dioxide and it shows the same theoretical level and basis set dependencies (Figure 3). Based on the carbon dioxide calculations and the derived *m*-parameter for Δα, we predict a "best estimate" of 14.2 au^3 for carbodiimide.

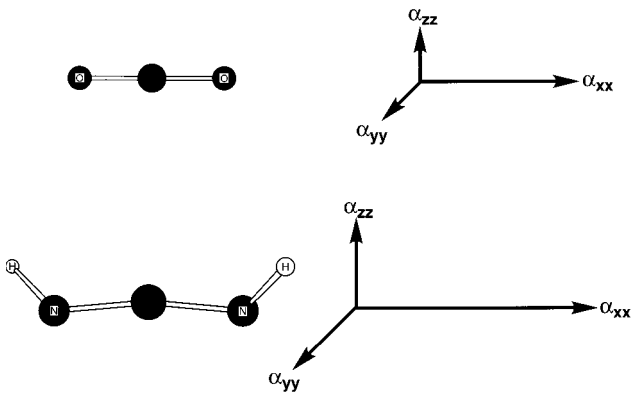
Polarizability Anisotropy κ. The theoretical level and basis set dependencies of the κ values of $C(NH)_2$ are illustrated in Figure 3. The calculated κ value of carbon dioxide is 0.29−0.42 au^3, and the basis set dependency is very different from what was seen for the three electric dipole polarizability tensor components, $\langle\alpha\rangle$ and Δα. Surprisingly, the effect of diffuse functions is minimal. However, there is a pronounced basis set effect in that the number of d-type polarization functions determines the quality of the result. When a second set of d-functions is added to the basis set, there is a sharp decrease of 0.7−0.8 au^3 in the value of κ, and there is a second sharp decrease upon addition of a third set of more diffuse d-functions. Further polarization with f-functions does not affect κ very much. For the calculation of κ, the choice of basis set is more important than the choice of method; using the best basis sets, the RHF calculated value is approximately 0.260 au^3 and the electron-correlation value is about 0.289 au^3. Once again, the MP2 and QCISD methods give essentially the same results. The experimental κ value of carbon dioxide is 0.267 au^3 and the QCISD/6-311+G(3df,2pd) calculated value is about 8% too high.

The polarizability anisotropy κ of carbodiimide is not known even though it is a measurable value. The theoretical model and basis set dependencies (Figure 3) are similar to those for carbon dioxide. The calculated value of κ at QCISD/6-311++G(3df,2pd) is 0.31 au^3 and, considering the *m*-parameter for κ, we predict a best estimate of 0.286 au^3.

Conclusion

Our studies have revealed several important basis set dependencies and we offered explanations for these basis set effects. The effects of diffuse functions are pronounced at every theoretical level, and the addition of diffuse functions greatly increases *all* of the polarizability tensor components. To a large degree, polarizability is mediated by the spatially extended electron density and the diffuse functions are needed to adequately describe this electron density. Comparison of the α_{xx} electric dipole polarizability tensor component with the experimental value of carbon dioxide shows that this value is accurately reproduced at the electron-correlated levels when diffuse functions are incorporated into the basis set. However, basis set augmentation by diffuse functions alone does not

SCHEME 2: Polarizabilities of Carbon Dioxide and Carbodiimide



suffice to compute accurate values of the α_{yy} and α_{zz} tensor components. The α_{yy} and α_{zz} tensor components reflect properties of the π-electron density of the heterocumulenes. This π-electron density is highly polarized and its accurate description requires suitable polarization functions. Our studies show in a compelling fashion (Figure 2) that polarization by way of a single or even a double set of d-functions does not polarize the electron density described by the two outermost p-functions. The third set of d-functions is essential to polarize the outer electron density. Without the polarization of the diffuse functions by the third set of spatially extended d-functions, the α_{yy} and α_{zz} tensor components cannot be accurately reproduced.

The polarizability parameters $\langle\alpha\rangle$ and $\Delta\alpha$ all show significant basis set dependencies because the components $\alpha_{||}$ and $\alpha_{\perp}$ very much depend on the presence of diffuse functions and the augmentation by three d-polarization functions. For the anisotropic polarizability κ, we find a striking effect in that the quality of the κ values is dominated by the number of sets of d-polarization functions. There are clear breaks in the theoretical level dependency of this anisotropy quantity in going from (d) to (2d) and then again from (2d) to (3d).

The electric dipole polarizability calculations show hardly any significant difference between the results obtained using the MP2 perturbation method and the much more expensive iterative QCISD method. This finding is very important with a view to computational studies of larger systems. QCISD calculations not only are very expensive and computer-time intensive, but in fact they are impossible for even mid-sized molecules.

The molecular isotropic polarizability of carbodiimide is almost twice that of carbon dioxide in every Cartesian direction. This is illustrated in Scheme 2 with the vectoral representation of the α_{xx}, α_{yy}, and α_{zz} tensor components. Our calculations and accuracy assessments lead us to the following predictions for carbodiimide: $\langle\alpha\rangle = 30.8$ au^3 and $\kappa = 0.286$ au^3.

Supporting Information Available: Extended versions of Tables 1 and 2 with all the data determined at all theoretical levels and figures illustrating the theoretical level dependencies for carbon dioxide. This material is available free of charge via the Internet at http://pubs.acs.org.

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