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Determination of the Complete Polarizability Tensor of 1,3-Butadiene by Combination of Refractive Index and Light Scattering Measurements and Accurate Quantum Chemical ab Initio Calculations

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We have combined accurate quantum chemical calculations and light scattering measurements to obtain a reliable estimate of the electric dipole polarizability anisotropy of 1,3-butadiene. The theoretical investigation was based on finite-field many-body perturbation theory and coupled cluster techniques. An extensive study of basis set, electron correlation, and molecular geometry effects leads to a static value of $\alpha = 54.04\ e^2a_0^2E_h^{-1}$ for the mean dipole polarizability of *trans*-butadiene, in very good agreement with the experimental result of $54.64\ e^2a_0^2E_h^{-1}$ obtained from an extrapolation to infinite wavelength of refractivity data [Hohm, U.; Trümper, U. *Ber. Bunsenges. Phys. Chem*. **1992**, *96*, 1061]. The measured value of the dipole polarizability anisotropy of *trans*-butadiene is $42.5(1.7)\ e^2a_0^2E_h^{-1}$ at 514.5 nm. To our knowledge, these are the first light-scattering experiments to be reported for 1,3-butadiene. The present investigation brings forth new possibilities for the extension of accurate determination of electric polarizabilities to molecules of some size. *cis*-Butadiene is less polarizable and less anisotropic than the trans isomer.

Introduction

The rational approach to the interpretation of a wide range of phenomena relies almost exclusively on the accurate determination of the distortion of atoms and molecules in the presence of an electric field.[1] The theory of electric polarizability reduces the description of these distortions to permanent molecular properties, the electric polarizabilities, and hyperpolarizabilities. Of all these properties the dipole polarizability emerges as one of universal importance. In addition to classes of phenomena related to intermolecular interactions,[2] electron scattering,[3] and optics,[4] the dipole polarizability is also linked to atomic/molecular characteristics as softness and hardness[5] and electronegativity.[6] The experimental and theoretical determination of dipole polarizabilities is currently a field expanding with considerable force.[7]

In this paper we focus our attention on 1,3-butadiene, an important substance in many fields of natural sciences ranging from chemical technology[8] to photoelectron spectroscopy.[9] In addition, the current interest in the optics of polyene chains has prompted several investigations of the electric properties of such systems.[10,11] Understandably, its physicochemical properties should be known as accurately as possible. However, an examination of the available values reveals inconsistencies that may be attributed to a variety of reasons. Gas-phase measurements of the dispersion of the mean dipole polarizability[12] and rigorous quantum chemical studies by Karna et al.,[13] Norman et al.,[14] and Rozyczko et al.[15] based on ab initio calculations do not display entirely satisfactory agreement. Therefore, we decided to obtain an accurate description of the dipole polarizability tensor $\hat{\alpha}$ of 1,3-butadiene by combination of refractive index measurements, light-scattering experiments, and quantum chemical ab initio calculations. To obtain information about the noninteracting molecule, all measurements are carried out in the gas phase. In the quantum chemical part of this endeavor we consider all factors affecting the quality of the theoretical predictions. Basis set and electron correlation effects, the dependence of the calculated polarizabilities on the molecular geometry, are carefully examined and analyzed.

Theory

General Theoretical Considerations. If a molecule is placed in a very weak, homogeneous electric field $\vec{E}$, it acquires a dipole moment $\vec{\mu}$,

$$\vec{\mu} \cong \hat{\alpha} \cdot \vec{E} \qquad (1)$$

where $\hat{\alpha}$ is the dipole−dipole polarizability tensor. The invariants of $\hat{\alpha}$ are the mean dipole polarizability α and the dipole polarizability anisotropy $\Delta\alpha$, which are given as (x, y, and z refer to the principal axes of the molecule)

$$\alpha = \frac{1}{3}(\alpha_{xx} + \alpha_{yy} + \alpha_{zz}) \qquad (2)$$

$$(\Delta\alpha)^2 = \left[\frac{1}{2}(3\hat{\alpha}:\hat{\alpha} - 9\alpha^2)\right] \qquad (3)$$

In the case of low-density gases α and $\Delta\alpha$ are related in a simple way to the refractive index $n(\omega,d,T)$ and the depolar-

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ization ratio $\rho(\omega)$, where ω is the frequency of the light, d is the density, and T the temperature.

$$n(\omega,d,T) - 1 = \frac{N_A}{2\epsilon_0}\alpha(\omega)d \tag{4}$$

$$\rho(\omega) = \frac{I^H}{I^V} = \frac{3\Delta\alpha^2(\omega)}{45\alpha^2(\omega) + 4\Delta\alpha^2(\omega)} \tag{5}$$

In eq 4 it is assumed that the light is scattered at right angle and that the scattered intensities I^H (depolarized component) and I^V (polarized component) include only the Rayleigh (=unshifted) and rotational Raman lines. These requirements have been discussed in detail by Bridge and Buckingham.[16] With regard to eqs 4 and 5, combination of refractive index and light-scattering experiments provides a suitable method for obtaining the polarizability anisotropy of molecules.

Computational Strategy

The calculation of the dipole polarizability of butadiene in this paper relies on the finite-field method.[17] More detailed descriptions of our method and emphasis on the computational aspects may be found in previous work.[18-25] The energy of an uncharged molecule in a homogeneous electric field can be written as[1,26]

$$E^p = E^0 - \mu_\alpha F_\alpha - (1/2)\alpha_{\alpha\beta}F_\alpha F_\beta - (1/6)\beta_{\alpha\beta\gamma}F_\alpha F_\beta F_\gamma - (1/24)\gamma_{\alpha\beta\gamma\delta}F_\alpha F_\beta F_\gamma F_\delta + ... \tag{6}$$

where E^0 is the energy of the unperturbed molecule, F_α the field at the origin, and μ_α, $\alpha_{\alpha\beta}$, $\beta_{\alpha\beta\gamma}$, and $\gamma_{\alpha\beta\gamma\delta}$ the dipole moment, polarizability, and dipole hyperpolarizabilities (the repeated Greek subscript implies summation over the Cartesian coordinates x, y, and z). For molecules with C_{2h} (*trans*-1,3-butadiene) symmetry the dipole polarizability tensor $\alpha_{\alpha\beta}$ has four independent components and for C_{2v} symmetry (*cis*-1,3-butadiene) three.[1] Adopting the molecular orientation shown in Figure 1, we specify the dipole polarizability of *trans*-butadiene by the α_{xx}, α_{yy}, α_{zz}, and α_{xz} components. For *cis*-butadiene the respective components are α_{xx}, α_{yy}, and α_{zz}. It should be noted that *cis*-butadiene has a permanent dipole moment along the x axis. Thus, using very weak fields, eq 6 reduces to

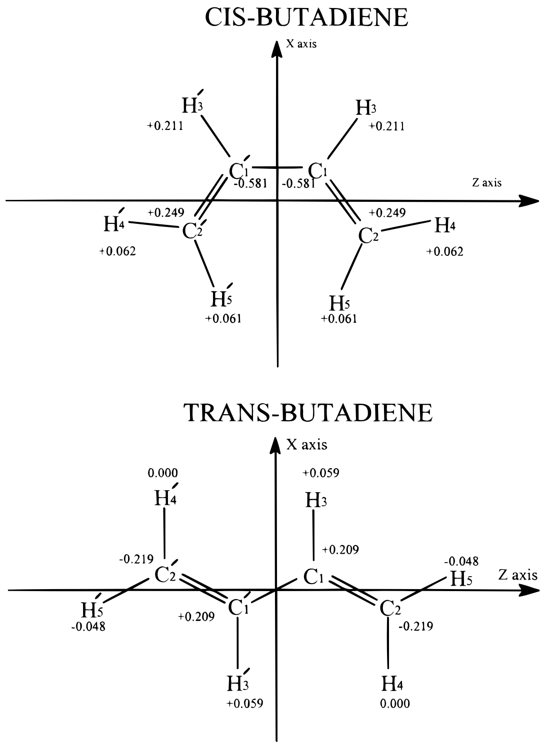
$$\begin{aligned} E(F_x,0,0) &\approx E^0 - \mu_x F_x - (1/2)\alpha_{xx}F_x^{\,2} \\ E(0,F_y,0) &\approx E^0 - (1/2)\alpha_{yy}F_y^{\,2} \\ E(0,0,F_z) &\approx E^0 - (1/2)\alpha_{zz}F_z^{\,2} \end{aligned} \tag{7}$$

for *cis*-butadiene. Fields of strength 0, $\pm F_x$, F_y, and F_z are applied, and the relevant dipole moment and polarizability components are extracted from the perturbed molecular energies. For *trans*-butadiene $\mu_\alpha = \beta_{\alpha\beta\gamma} = 0$ and

$$E^p \approx E^0 - (1/2)\alpha_{\alpha\beta}F_\alpha F_\beta \tag{8}$$

The α_{xx}, α_{yy}, and α_{zz} components are obtained from calculations with electric fields 0, F_x, F_y, and F_z, while α_{xz} is obtained from calculations with cross fields.

Equations 7 and 8 are used for the calculation of self-consistent field (SCF) and correlated calculations. Electron correlation effects are accounted for via many-body perturbation theory (MP) and coupled cluster techniques (CC). A detailed presentation of these powerful computational tools may be found elsewhere.[27-33] We emphasize the point that we lean heavily on the predictive capability of CC techniques[34-36] in order to reach reliable conclusions. We use the computationally less expensive MP techniques whenever CC calculations are not feasible. The most accurate method used in this work is CCSD(T), single and double excitation coupled cluster theory with an estimate of connected triple excitations obtained via a perturbational treatment. We use a uniform notation for the energy, the dipole moment, and the polarizability components. Thus, for the CC methods,


CIS-BUTADIENE

TRANS-BUTADIENE

Figure 1. Molecular geometry of *cis*- and *trans*-butadiene with atomic charges obtained from a Mulliken population analysis with a near-Hartree-Fock quality basis set (GI molecular geometry; see text).

$$\mathrm{CCSD(T)} = \mathrm{CCSD} + \mathrm{T} \tag{9}$$

The various orders of MP are hierarchically defined as

$$\begin{aligned} \mathrm{MP2} &= \mathrm{SCF} + \mathrm{D2} \\ \mathrm{MP3} &= \mathrm{MP2} + \mathrm{D3} \\ \mathrm{DQ\text{-}MP4} &= \mathrm{MP3} + \mathrm{D4} + \mathrm{QR4} = \mathrm{MP3} + \mathrm{DQ4} \\ \mathrm{SDQ\text{-}MP4} &= \mathrm{DQ\text{-}MP4} + \mathrm{S4} \\ \mathrm{MP4} &= \mathrm{SDQ\text{-}MP4} + \mathrm{T4} \\ &\equiv \mathrm{SCF} + \mathrm{D2} + \mathrm{D3} + \mathrm{S4} + \mathrm{D4} + \mathrm{T4} + \mathrm{Q4} + \mathrm{R4} \end{aligned} \tag{10}$$

The fourth-order terms in eq 10 are contributions from single (S4), double (D4), triple (T4), and quadruple (Q4) substitutions from the reference zeroth-order wave function, and R4 is the renormalization term.

It is obvious that similar expansions hold for the mean dipole polarizability α, since it is defined as a linear combination of α_{xx}, α_{yy}, and α_{zz}. The anisotropy $\Delta\alpha$, defined by eq 3 or more explicitly as

$$\Delta\alpha = (1/2)^{1/2}[(\alpha_{xx} - \alpha_{yy})^2 + (\alpha_{yy} - \alpha_{zz})^2 + (\alpha_{zz} - \alpha_{xx})^2 + 6\alpha_{xz}^{\,2}]^{1/2} \tag{11}$$

TABLE 1: Dipole Polarizability of *cis*-Butadiene Obtained at the GI Geometry (See Text)[a]

basis set	method	μ_z	α_{xx}	α_{yy}	α_{zz}	α	$\Delta\alpha$
C0 [5s3p2d/3s2p]	SCF	0.009	52.06	36.23	66.21	51.50	25.97
	MP2	0.012	51.32	36.45	64.05	50.61	23.92
	MP3	0.019	50.76	35.66	62.38	49.60	23.21
	DQ-MP4	0.015	50.53	35.35	61.53	49.14	22.76
	SDQ-MP4	0.016	50.88	35.40	62.33	49.54	23.41
	MP4	0.017	51.28	35.96	63.48	50.24	23.89
	CCSD	0.015	50.78	35.34	62.30	49.47	23.44
	CCSD(T)	0.016	51.03	35.68	63.04	49.92	23.75
C1 [5s3p2d/3s2p1d]	SCF	0.008	52.04	36.28	66.22	51.52	25.94
	MP2	0.018	51.38	36.51	64.20	50.70	24.00
	MP3	0.024	50.81	35.68	62.54	49.67	23.32
	DQ-MP4	0.020	50.57	35.37	61.69	49.21	22.88
	SDQ-MP4	0.021	50.92	35.42	62.48	49.61	23.52
	MP4	0.022	51.33	36.00	63.65	50.33	24.00
C2 [5s3p3d1f/3s2p1d]	SCF	0.007	52.26	36.26	66.67	51.73	26.35

[a] All values in atomic units. Conversion factors to SI units: dipole moment μ, 1 $ea_0 = 8.478358 \times 10^{-30}$ C m; dipole polarizability α, 1 $e^2a_0^2E_h^{-1} = 1.648778 \times 10^{-41}$ C^2 m^2 J^{-1}.

will be obtained at any level of theory by inserting in eq 11 the relevant quantities for α_{xx}, α_{yy}, α_{zz}, and α_{xz}.

All calculations in this work were performed with the Gaussian 92[37] and Gaussian 94[38] programs.

Basis Sets. It is hard to overemphasize the importance of basis set selection in polarizability calculations. Various aspects of this subject have been brought forth by many authors.[39−43] In this work we have used as a starting point a substrate consisting of a (9s6p) primitive set of Gaussian type functions (GTF) contracted to [4s2p] for carbon and a (4s)[2s] set for hydrogen.[44] The performance of this substrate has been successfully tested in previous work.[45−49] Butadiene is a fairly large molecule. We have performed a very detailed optimization in order to obtain the best possible results in the most economical way. The initial substrate of [4s2p/2s] was augmented to [5s3p/3s] by adding diffuse s- and p-GTF on both atoms. Next, we added d-GTF on carbon and p-GTF on hydrogen with exponents chosen to minimize the total energy of the molecule. The resulting [5s3p1d/3s1p] basis set was further augmented to [5s3p2d/3s2p] with d-GTF (C) and p-GTF (H) with exponents chosen to maximize the mean dipole polarizability α. The exponents of the added GTF are not the same for all carbon or hydrogen atoms. The optimization proceeded systematically for all equivalent pairs of atoms (see Figure 1). We started from the C_1,C_1' pair, proceeded to C_2,C_2', and continued with the hydrogen atom pairs H_3,H_3', then H_4,H_4', and finally H_5,H_5'. The optimization produced two basis sets C0 for *cis*-butadiene and T0 for *trans*-butadiene, both consisting of 150 CGTF. These basis sets are fully presented in Table 7. From C0 and T0 we derived C1 and T1 by adding on all hydrogen atoms one d-GTF with exponent equal to that of the most diffuse (that is, optimized for α) p-GTF. The largest basis set for both isomers is [5s3p3d1f/3s2p1d], consisting of 228 CGTF. This set is obtained from C1 and T1 by adding d-GTF on all carbon atoms with exponents computed as

$$\eta_d = \eta_d(\text{diffuse})\left(\frac{\eta_d(\text{diffuse})}{\eta_d(\text{tight})}\right)^{1/2} \tag{12}$$

The η_d(tight) and η_d(diffuse) in eq 12 are the exponents of the d-GTF on carbon optimized for the total energy and the mean dipole polarizability, respectively, as described above. Two additional basis sets were constructed for *trans*-butadiene, T01 ≡ [5s3p3d/3s2p] and T02 ≡ [5s3p3d/3s3p]. Both basis sets were obtained from T0 following the algorithm of eq 12 for the d-GTF on carbon or a similar one for the p-GTF on hydrogen.

Molecular Geometries. All calculations for *cis*-butadiene were performed at the theoretical geometry calculated by Kirtman et al.[50] defined by $R(C_1{-}C_1') = 1.483$ Å, $R(C_1{-}C_2) = 1.321$ Å, $R(C_1{-}H_3) = 1.081$ Å, $R(C_2{-}H_4) = 1.078$ Å, $R(C_2{-}H_5) = 1.079$ Å, $\angle(C_1'{-}C_1{-}H_3) = 115.3°$, $\angle(C_1'{-}C_1{-}C_2) = 125.5°$, $\angle(C_1{-}C_2{-}H_5) = 122.2°$, and $\angle(H_5{-}C_2{-}H_4) = 116.0°$. This geometry, either for the cis or the trans isomer, is denoted as GI.

The molecular geometry of *trans*-butadiene has attracted considerable attention. Molecular property calculations pertain to theoretically determined geometries, sets of data derived partially from experimental efforts or model geometries. This diversity renders comparisons of polarizability data extremely difficult. The GI geometry for *trans*-butadiene[50] is defined as $R(C_1{-}C_1') = 1.468$ Å, $R(C_1{-}C_2) = 1.321$ Å, $R(C_1{-}H_3) = 1.080$ Å, $R(C_2{-}H_4) = 1.081$ Å, $R(C_2{-}H_5) = 1.079$ Å, $\angle(C_1'{-}C_1{-}H_3) = 116.3°$, $\angle(C_1'{-}C_1{-}C_2) = 124.1°$, $\angle(C_1{-}C_2{-}H_5) = 122.0°$, and $\angle(H_5{-}C_2{-}H_4) = 116.2°$. We have adopted the experimental geometry of Haugen and Traetteberg,[51] as it has been used by many authors. This geometry is defined by $R(C_1{-}C_1') = 1.467$ Å, $R(C_1{-}C_2) = 1.343$ Å, $R(C{-}H) = 1.094$ Å, $\angle(C_1'{-}C_1{-}H_3) = 117.7°$, $\angle(C_1'{-}C_1{-}C_2) = 122.8°$, and $\angle(C_1{-}C_2{-}H_5) = 119.5°$. This geometry is denoted as GII. We have also obtained a third molecular geometry at the MP2/[5s3p1d/3s1p] level of theory, where the [5s3p1d/3s1p] basis set has been obtained from T0 by deleting the most diffuse d-GTF on carbon and the most diffuse p-GTF on hydrogen. This geometry, denoted GIII, is defined by $R(C_1{-}C_1') = 1.4618$ Å, $R(C_1{-}C_2) = 1.3516$ Å, $R(C_1{-}H_3) = 1.0868$ Å, $R(C_2{-}H_4) = 1.0833$ Å, $R(C_2{-}H_5) = 1.0813$ Å, $\angle(C_1'{-}C_1{-}H_3) = 117.0°$, $\angle(C_1'{-}C_1{-}C_2) = 123.5°$, $\angle(C_1{-}C_2{-}H_5) = 121.5°$, and $\angle(H_5{-}C_2{-}H_4) = 117.5°$.

We judge it worth mentioning that other experimental geometries present small differences for certain parameters.[52−54] An interesting study of the molecular geometry of *trans*-butadiene has been reported by Brunger et al.[55]

Ab Initio Results. *cis-Butadiene*. The molecular properties of *cis*-butadiene were calculated at the GI geometry and are displayed in Table 1. We also show in Figure 1 the results of a Mulliken population analysis obtained with basis C2 at the GI geometry, a strong indication of the complexity of the charge distribution for such a polyatomic molecule. CCSD(T) calculations were performed with C0, MP4 with C1, and SCF with the large C2 basis set. We expect the C2 basis set to yield SCF values close to the Hartree−Fock limit for all properties. The C2 values for μ_z/ea_0 and $\alpha_{\alpha\beta}/e^2a_0^2E_h^{-1}$ are $\mu_z = 0.007$, $\alpha_{xx} =$

TABLE 2: Analysis of Electron Correlation Effects on the Dipole Polarizability ($\alpha_{\alpha\beta}/e^2a_0^2E_h^{-1}$) of *trans*-Butadiene at the Experimental Molecular Geometry (GII; See Text)[a]

method	α_{xx}	α_{yy}	α_{zz}	α_{xz}	α	$\Delta\alpha$
SCF	48.20	37.70	85.35	−12.35	57.08	48.35
D2	−0.10	0.00	−6.74	4.39	−2.28	
D3	−0.56	−0.81	−2.06	−0.14	−1.14	
S4	0.35	0.05	1.37	−0.42	0.59	
D4	−0.22	−0.21	−1.66	0.64	−0.70	
T4	0.44	0.57	1.27	0.27	0.76	
QR4	0.00	−0.11	0.43	−0.47	0.11	
ΔCCSD	−0.56	−1.15	−8.69	3.84	−3.47	
T	0.35	0.33	0.59	0.29	0.42	
MP2	48.09	37.70	78.61	−7.96	54.80	39.32
MP3	47.54	36.89	76.55	−8.10	53.66	38.22
DQ-MP4	47.31	36.57	75.32	−7.92	53.07	37.27
SDQ-MP4	47.66	36.62	76.69	−8.35	53.66	38.65
MP4	48.10	37.20	77.96	−8.08	54.42	39.13
CCSD	47.63	36.56	76.65	−8.51	53.61	38.78
CCSD(T)	47.99	36.89	77.24	−8.22	54.04	38.81

[a] Basis set T0 ≡ [5s3p2d/3s2p] (150 CGTF). The four innermost molecular orbitals were kept frozen. All values in atomic units.

TABLE 3: Dependence of the Dipole Polarizability of *trans*-Butadiene on the Length of the C=C Bond around its Experimental Value of 1.343 Å[a]

$(R_{C=C} - 1.343)$/Å	α_{xx}	α_{yy}	α_{zz}	α_{xz}	α	$\Delta\alpha$
−0.10	46.09	34.11	70.59	−8.77	50.26	35.61
−0.05	47.09	35.88	77.38	−10.44	53.45	41.34
0	48.20	37.70	85.35	−12.35	57.08	48.35
0.05	49.38	39.55	94.64	−14.52	61.19	56.76
0.10	50.64	41.42	105.43	−16.95	65.83	66.74

[a] All other parameters of the GII geometry were kept fixed. SCF results calculated with basis set T0 ≡ [5s3p2d/3s2p]. All values in atomic units.

TABLE 4: Dependence of the Dipole Polarizability of *trans*-Butadiene on the Length of the C−C Bond around its Experimental Value of 1.467 Å[a]

$(R_{C-C} - 1.467)$/Å	α_{xx}	α_{yy}	α_{zz}	α_{xz}	α	$\Delta\alpha$
−0.10	47.53	37.35	90.05	−12.98	58.31	53.38
−0.05	47.86	37.53	87.43	−12.66	57.60	50.62
0	48.20	37.70	85.35	−12.35	57.08	48.35
0.05	48.55	37.88	83.79	−12.04	56.74	46.55
0.10	48.90	38.05	82.74	−11.73	56.56	45.20

[a] All other parameters of the GII geometry were kept fixed. SCF results calculated with basis set T0 ≡ [5s3p2d/3s2p]. All values in atomic units.

52.26, $\alpha_{yy} = 36.26$, $\alpha_{zz} = 66.67$, $\alpha = 51.73$, and $\Delta\alpha = 26.35$. The C0 and C1 give SCF values very close to the above. Agreement is significantly better than 1% for all components of the dipole polarizability. Electron correlation doubles the dipole moment of *cis*-butadiene, but the final value is very small, close to 0.02. The effect is of the opposite sign for the dipole polarizability. The CCSD(T)/C0 values $\alpha_{xx} = 51.03$, $\alpha_{yy} = 35.68$, $\alpha_{zz} = 63.04$ are 1.4, 1.5, and 4.8%, respectively, lower than the SCF values of values $\alpha_{xx} = 52.06$, $\alpha_{yy} = 36.23$, $\alpha_{zz} = 66.21$. Consequently, a small reduction is also observed for the mean α and the anisotropy $\Delta\alpha$. The enlargement of the C0 basis set to C1 does not entail a significant change for the electron correlation effects of the dipole polarizability of *cis*-butadiene.

trans-Butadiene. Our efforts for *trans*-butadiene comprise calculations with five basis sets (T0, T01, T02, T1, and T2) at three molecular geometries (GI, GII, and GIII). CCSD(T) calculations were performed with basis T0 at all three geometries. The results of a Mulliken population analysis obtained with basis T0 at the GI geometry are shown in Figure 1.[56] In Table 2 we present an analysis of electron correlation effects obtained with T0 at the CCSD(T) level of theory and the GII geometry. We have examined closely the dependence of the dipole polarizability on the length of the C=C (Table 3) and C−C (Table 4) bonds, keeping all other molecular parameters fixed in both cases. In Table 5 we have collected a large amount of data for the electron correlation effects on the dipole polarizability at all three geometries. A first comparison of the results for the GI geometry indicates that *trans*-butadiene is more polarizable and more anisotropic than the cis isomer. For all three geometries, T2 should be expected to provide reliable SCF results, close to the respective Hartree−Fock limits. For GII we have employed five basis sets. The SCF mean dipole polarizabilities are $\alpha/e^2a_0^2E_h^{-1} = 57.08$ (T0), 57.29 (T01), 57.26 (T02), 57.12 (T1), and 57.34 (T2). The maximum difference is 0.26, representing an agreement better than 1% in all cases. For the anisotropy $\Delta\alpha/e^2a_0^2E_h^{-1} = 48.35$ (T0), 48.57 (T01), 48.53 (T02), 48.47 (T1), and 48.49 (T2). The stability of these values ($\Delta\alpha$ is a quantity more basis set sensitive than α) supports strongly our claim to near-Hartree−Fock quality for the basis sets constructed in this work.

The analysis of the electron correlation effects on the components of the dipole polarizability of *trans*-butadiene for the experimental geometry GII reveals several important facts. Electron correlation reduces α_{xx}, α_{yy}, and α_{zz} and the magnitude of the negative α_{xz}. The convergence of the MP series is satisfactory for the α_{zz} but very slow for the other two components α_{xx} and α_{yy}. The total second-, third-, and fourth-order MP correction for the out-of-plane component $\alpha_{yy}/e^2a_0^2E_h^{-1}$ is 0.00, −0.81, and 0.30, respectively. The CCSD(T) value of α_{yy} is 36.89, just 2.1% lower than the SCF result of 37.70 $e^2a_0^2E_h^{-1}$. The effect is even smaller for the α_{xx} component. Overall, at GII, the mean polarizability $\alpha/e^2a_0^2E_h^{-1}$ decreases from 57.08 (SCF) to 54.04 (CCSD(T)), a reduction of 5.4%. The reduction is more important for the anisotropy $\Delta\alpha$. The CCSD(T) value is 38.81, or 19.7% lower than the SCF of 48.35 $e^2a_0^2E_h^{-1}$. Extending our observations, we note that the total electron correlation correction ECC = CCSD(T) − SCF for the mean polarizability $\alpha/e^2a_0^2E_h^{-1}$ varies with the molecular geometry as −2.48 (GI), −3.04 (GII), and −3.41 (GIII). For the anisotropy $\Delta\alpha/e^2a_0^2E_h^{-1}$ we have −8.28 (GI), −9.54 (GII), and −10.14 (GIII). This strong dependence of the ECC on the molecular geometry renders the comparison of theoretical values calculated at significantly different geometries difficult if not meaningless. To complete this part of the discussion, we consider the effect of specific molecular geometry parameters on the dipole polarizability. In Table 3 we display SCF/T0 values calculated at five different C=C bond lengths, with the experimental value as reference and keeping all other parameters fixed. We see that the component most affected is α_{zz}, varying from 70.59 to 105.43 $e^2a_0^2E_h^{-1}$. The mean increases strongly, but the increase of the anisotropy is even more impressive. Their variation with respect to C=C bond length change is (all quantities in atomic units)

$$\alpha(R_{C=C})/e^2a_0^2E_h^{-1} = 57.08 + 40.88\Delta R + 27.04\Delta R^2 + 8.89\Delta R^3 \quad (13)$$

$$\Delta\alpha(R_{C=C})/e^2a_0^2E_h^{-1} = 48.35 + 81.34\Delta R + 79.21\Delta R^2 + 28.65\Delta R^3 \quad (14)$$

where $\Delta R \equiv R_{C=C} - 2.537902$ in a_0.

The dependence of the dipole polarizability on the C−C bond length (Table 4) is less pronounced. Both α and $\Delta\alpha$ decrease with R_{C-C} and

TABLE 5: Basis Set and Electron Correlation Effects on the Dipole Polarizability of *trans*-Butadiene for All Molecular Geometries Considered in This Work[a]

basis set	method	α_{xx}	α_{yy}	α_{zz}	α_{xz}	α	$\Delta\alpha$
Molecular Geometry GI							
T0 [5s3p2d/3s2p]	SCF	46.69	36.79	82.16	−11.99	55.21	46.25
	MP4	46.46	36.28	74.92	−8.24	52.55	38.32
	CCSD	46.34	35.82	74.75	−8.60	52.30	37.92
	CCSD(T)	46.69	36.16	75.34	−8.34	52.73	37.97
T1 [5s3p2d/3s2p1d]	SCF	46.63	36.82	82.28	−11.99	55.24	46.35
	MP4	46.81	36.48	76.34	−8.26	53.21	38.57
T2 [5s3p3d1f/3s2p1d]	SCF	46.97	36.85	82.51	−11.90	55.44	46.37
Molecular Geometry GII							
T0 [5s3p2d/3s2p]	SCF	48.20	37.70	85.35	−12.35	57.08	48.35
	MP4	48.10	37.20	77.96	−8.08	54.42	39.13
	CCSD	47.63	36.56	76.65	−8.51	53.61	38.78
	CCSD(T)	47.99	36.89	77.24	−8.22	54.04	38.81
T01 [5s3p3d/3s2p]	SCF	48.54	37.65	85.66	−12.36	57.29	48.57
	MP4	48.38	37.27	78.19	−8.02	54.61	39.20
T02 [5s3p3d/3s3p]	SCF	48.50	37.67	85.62	−12.36	57.26	48.53
	SDQ-MP4	47.84	36.73	76.92	−8.35	53.83	38.75
T1 [5s3p2d/3s2p1d]	SCF	48.15	37.74	85.48	−12.37	57.12	48.47
	MP4	48.10	37.23	78.25	−8.10	54.53	39.39
T2 [5s3p3d1f/3s2p1d]	SCF	48.51	37.78	85.73	−12.26	57.34	48.49
Molecular Geometry GIII							
T0 [5s3p2d/3s2p]	SCF	47.67	37.91	87.27	−13.12	57.62	50.66
	MP4	47.49	37.27	79.01	−8.59	54.59	38.52
	CCSD	47.04	36.64	77.75	−9.05	53.81	40.02
	CCSD(T)	47.38	36.96	78.30	−8.74	54.21	40.52
T2 [5s3p3d1f/3s2p1d]	SCF	48.00	37.98	87.65	−13.03	57.88	50.78

[a] All values in atomic units.

$$\alpha(R_{\mathrm{C-C}})/e^2a_0^2E_\mathrm{h}^{-1} = 57.08 - 4.52\Delta R + 9.92\Delta R^2 - 2.96\Delta R^3 \quad (15)$$

$$\Delta\alpha(R_{\mathrm{C-C}})/e^2a_0^2E_\mathrm{h}^{-1} = 48.35 - 21.50\Delta R + 26.32\Delta R^2 - 3.95\Delta R^3 \quad (16)$$

where $\Delta R = R_{\mathrm{C-C}} - 2.772228$ in a_0. Equations 13−16 provide strong indication that the C═C bond length affects strongly the dipole polarizability and that even small variations of this parameter might be responsible for significant changes in the calculated values.

Experiment

Experimental Setup. Depolarization ratios were measured at 514.5 nm using a Spectra Physics Ar$^+$ laser (model Stabilite 2017-06S) operated in the single-line mode. The beam diameter was 1.4 mm and the beam divergence 1.7′. Operating the laser in power mode gave a stability of ±0.5% of the output power. The output power was set between 200 and 1800 mW.

The beam was focused into the scattering volume using a biconvex lens (focal length of 50 cm). The resulting beam divergence is less than 10′ and, therefore, introduces a negligible error in ρ.[16] The plane of vibration of the incoming light can be rotated by 90° using a half-wave plate. The Glan−Thompson polarizer (extinction ratio of $<10^{-6}$) was rotated in the same manner so that either vertically or horizontally polarized laser light entered the scattering cell. The analyzer has an extinction ratio of better than 10^{-5} and remained fixed in the vertical position throughout all of the experiments. This procedure excluded errors caused by a different sensitivity of the photomultiplier tube and the monochromator with respect to the plane of polarization of the scattered light. The plane of polarization of the laser light and the relative positions of the polarizer and analyzer were determined with a method described by Couling.[57] The rest of the apparatus was a slightly modified conventional Raman spectrometer (model Coderg LRT800). The perpendicularly scattered light was collected by a lens and focused on the entrance slit of the triple monochromator, which was driven by an electronically controlled stepper motor. The minimum step width was $^1/_8$ cm^{-1}. The width of the entrance and exit slits of the monochromator were varied between 30 and 300 μm, and the two inner slits were fixed at 600 μm. The detection system consisted of an RCA C31034A photomultiplier tube (PMT) operating at 1550 V and cooled to −20 °C. We operated the system in the photon-counting mode. The linearity of the whole system used is ensured below 9000 counts/s. The laser power was adjusted accordingly.

The scattering cell was a cylinder 23 cm in length with an inner diameter of 3 cm. It was made of stainless steel. The three entrance and exit windows had a diameter of 1.25 cm and a thickness of 0.3 cm. To ensure a dark background of the field of view of the PMT, a Wood's horn, which was made out of blackened glass, was positioned opposite the viewing window. Four light baffles were placed inside the cell in order to reduce stray light produced by the scattering cell. Like Couling,[57] we did not use windows set under the Brewster angle for the entrance and exit of the laser beam. This setup is different from most other scattering cells used in these types of light-scattering experiments.[16,58−60] In our case the use of Brewster angle windows is clearly permitted by rotating the plane of polarization of the incoming laser beam rather than the scattered laser beam.

The light-scattering cell was connected via standard stainless steel tubing with a high-precision pressure transducer (model MKS-Baratron model 690A), vacuum pump (Edwards E2Ml.5), and the gas handling system. The gaseous samples were passed through a filter with a pore size of 0.5 μm (Nupro 6-TF) to ensure dust-free samples. The whole apparatus could be evacuated to less than 1 Pa. The temperature of the cell was determined by means of a standard NiCr−Ni thermocouple to ±0.l K.

Performance of the Measurements. The scattering cell was filled with the gaseous sample up to a maximum pressure $p_{\max}$ of 10^5 Pa. Argon (purity, >99.993%), krypton (purity, >99.99%), and 1,3-butadiene (purity, >99.5%), all supplied by Linde AG, Germany, were used without further purification. In the pressure range used, it was sufficient to calculate the density d of the gaseous samples according to

$$d = \left(\frac{p}{RT}\right)\left(1 - B(T)\left(\frac{p}{RT}\right)\right) \tag{17}$$

where p is the pressure, T the temperature, R the gas constant, and $B(T)$ is the second (p, V, T) virial coefficient. In the case of 1,3-butadiene, $B(T)$ was taken from Hohm and Trümper.[11] In the case of Ar and Kr, we use the tables given by Kerl.[61]

For each gas, spectrally resolved polarized and depolarized light-scattering spectra were recorded at six or seven different densities in the range between 0 and $d_{\max}$. To this end a range $\Delta\nu_{\min}-\Delta\nu_{\max}$ was scanned with a step width of the triple monochromator of $\Delta(\Delta\nu) = {}^1/_8\ \mathrm{cm}^{-1}$. $\Delta\nu = \nu_0 - \nu$ is measured relative to the excitation line. $\nu_0 = 19436.3\ \mathrm{cm}^{-1}$ is the wavenumber of the incoming laser light. The wavelength range scanned in our experiments was symmetric with respect to the laser line ($-\Delta\nu_{\min} = \Delta\nu_{\max}$). We chose $\Delta\nu_{\max}$ in accordance with the requirement that scattering due to rotational Raman lines is included, however scattering due to vibrational Raman lines is excluded in the recorded spectrum. The integration time at each wavenumber shift $\Delta\nu$ was 4 s. Each spectrum analyzed is the arithmetic mean of four recordings. The total recording time of the whole light-scattering spectrum at a given density d was four and a half hour.

Let $I^{(\mathrm{H,V})}(\Delta\nu,d)$ be the count rate recorded at density d and wavenumber shift $\Delta\nu$ in the horizontal (=depolarized, H) or vertical (=polarized, V) position of the polarizer. The integrated (=Rayleigh plus rotational Raman scattering) scattered intensity $I_{\mathrm{tot}}^{(\mathrm{H,V})}(\nu_0,d)$ is given by

$$I_{\mathrm{tot}}^{(\mathrm{H,V})}(\nu_0,d) = \int_{\Delta\nu_{\min}}^{\Delta\nu_{\max}} [I^{(\mathrm{H,V})}(\Delta\nu,d) - I_0^{(\mathrm{H,V})}(\Delta\nu,d)]\, \mathrm{d}(\Delta\nu) \tag{18}$$

where $I_0^{(\mathrm{H,V})}(\Delta\nu,d)$ is the background intensity. $I_0^{(\mathrm{H,V})}(\Delta\nu,d)$ includes mainly the dark-count of the photomultiplier tube. In all of our experiments a linear relationship between the total scattered intensity and the density according to

$$I_{\mathrm{tot}}^{(\mathrm{H,V})}(\nu_0,d) = A^{(\mathrm{H,V})}(\nu_0) + B^{(\mathrm{H,V})}(\nu_0)d \tag{19}$$

was obtained. Obviously, the sensitivity of our apparatus was not high enough in order to detect collision-induced effects at these low pressures, although the observation of collision-induced light-scattering of atoms and globular molecules at pressures around 1 atm has been reported by Watson and Rowell.[62]

The experimentally determined depolarization ratio $\rho_{\exp}(\nu_0)$ is calculated via the ratio

$$\rho_{\exp}(\nu_0) = \frac{B^{\mathrm{H}}(\nu_0)}{B^{\mathrm{V}}(\nu_0)} \tag{20}$$

where the coefficients $B^{\mathrm{H}}(\nu_0)$ and $B^{\mathrm{V}}(\nu_0)$ were determined by a least-squares fit analysis according to eq 19. Taking into account the experimentally determined nonvanishing depolarization ratio $\rho_0(\nu_0)$ of the noble gases Ar and Kr, we obtain the depolarization ratio $\rho(\nu_0)$ of the 1,3-butadiene sample via[63]

$$\rho(\nu_0) = \rho_{\exp}(\nu_0) - \rho_0(\nu_0) \tag{21}$$

Experimental Results

In contrast to most other experimental investigations of laser light scattered by gases[16,57−60,63−65] in our experiments, the scattered light is recorded spectrally resolved. This procedure ensures that contributions due to Rayleigh scattering and rotational Raman scattering are included in the scattered intensity and, on the other hand, that contributions due to vibrational Raman scattering are excluded. We did not use interference filters in order to delete vibrational Raman scattering. Rowell et al.[60] have pointed out that these filters can cause substantial loss of rotational Raman intensity, resulting in low depolarization ratio. However, this decrease was not detected by Keir.[59] After thorough alignment of the apparatus a depolarization ratio of $\rho_0(\nu_0) = 1.39(11) \times 10^{-3}$ was recorded for argon and krypton. This ratio was essentially the same for both of the two rare gases. ρ_0 was independent of the entrance and exit slit widths of the monochromator, which were varied between 50 and 300 μm. At the maximum pressure of 10^5 Pa the magnitude of $\rho_0(\nu_0)$ determined in our experiments is completely attributable to deficiencies of the scattering cell. Measurable contributions due to collision-induced light-scattering are known to occur at considerably higher densities. The $\rho_0(\nu_0)$ of the rare gases is much larger than reported by other investigators, where it ranges from 1.5×10^{-5} [64] to 2.8×10^{-4}.[58] The experimentally recorded ρ_0 may be due to small misalignment of the parallel entrance and exit windows of the scattering cell. Owing to the good reproducibility of $\rho_0(\nu_0)$, we use this quantity as a correction to the actual recorded scattered intensity $\rho_{\exp}(\nu_0)$ of 1,3-butadiene (see eq 21).

In the case of the 1,3-butadiene a slit width between 30 and 50 μm is used in our experiments. The laser power is adjusted to 1800 mW in the case of the depolar measurements and 200−400 mW in the case of the polar measurements. The maximum density used is $d \leq 40\ \mathrm{mol\ m}^{-3}$. The range of the wavenumber shift was set to $\Delta\nu_{\max} = 80\ \mathrm{cm}^{-1}$. A typical plot of the density and wavenumber-shift dependence of the depolarized scattered intensity $I^{\mathrm{H}}(\Delta\nu,d)$ is shown in Figure 2, and the resulting density dependence of the integrated total scattered intensity $I_{\mathrm{tot}}^{(\mathrm{H,V})}(\nu_0,d)$ is illustrated in Figure 3.

In total we have performed six independent measurements of the density dependence of the integrated scattered intensity $I_{\mathrm{tot}}^{(\mathrm{H,V})}(\nu_0,d)$ of 1,3-butadiene. From these measurements we obtain a mean measured depolarization ratio of $\rho_{\exp}(\nu_0) = 0.0354(25)$. With regard to eq 21 we yield the depolarization ratio of 1,3-butadiene as $\rho(\nu_0) = \rho_{\exp}(\nu_0) - \rho_0(\nu_0) = 0.0340(26)$. Once we know $\rho(\nu_0)$ and $\alpha(\nu_0)$, we are able to deduce the polarizability anisotropy $\Delta\alpha(\nu_0)$ of 1,3-butadiene. The frequency dependence of the mean dipole polarizability of 1,3-butadiene has been determined by Hohm and Trümper[12] in the wavelength range between 633 and 325 nm. From a fit of the polarizability data we obtain a mean dipole polarizability of $\alpha(\nu_0) = 58.166(58)\ e^2a_0{}^2E_{\mathrm{h}}{}^{-1}$. According to eq 4, a polarizability anisotropy of $\Delta\alpha(\nu_0) = 42.5(1.7)\ e^2a_0{}^2E_{\mathrm{h}}{}^{-1}$ is obtained for gaseous 1,3-butadiene at $T \approx 296$ K and wavenumber $\nu_0 = 19436.3\ \mathrm{cm}^{-1}$.

Our light-scattering and refractive index measurements[12] were carried out with an equilibrium mixture of *trans*- and *cis*-1,3-butadiene. However, there is strong evidence that at the temperatures used in our experiments ($T \approx 296$ K) the concentration of *cis*-1,3-butadiene is very low. This species has been detected neither in photoelectron spectroscopic experiments[9,66] nor in rotational Raman spectra.[67,68] Additionally, we did not observe the strong and polarized vibrational Raman

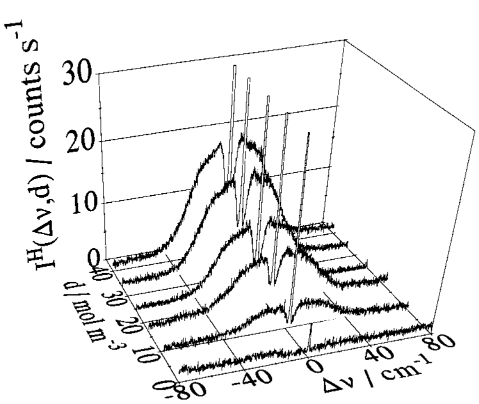


Figure 2. Depolarized light-scattering spectra of 1,3-butadiene recorded at $T \approx 296$ K.

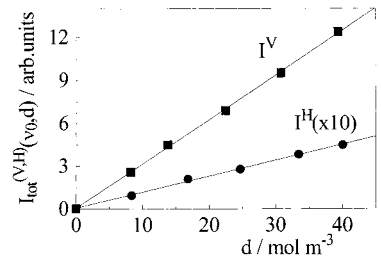


Figure 3. Density dependence of the integrated scattered intensity $I_{\mathrm{tot}}^{(\mathrm{H,V})}(\nu_0,d)$ of 1,3-butadiene: (■) polarized scattered intensity (I^{V}); (●) depolarized scattered intensity (I^{H}). The latter was obtained from the curve shown in Figure 2. The solid lines were calculated from linear least-squares fits.

transition of *cis*-1,3-butadiene, which should be present in the vicinity of $\Delta\nu = 200$ cm^{-1}.[69] It has been shown by Squillacote et al.[70] that thermally generated *cis*-1,3-butadiene trapped at 30 K rapidly transforms into *trans*-1,3-butadiene when heated to 60 K. From experimental investigations and theoretical calculations it can be concluded that the energy difference between *cis*- and *trans*-l,3-butadiene falls in the range between 10.4 and 13.0 kJ mol^{-1}.[70] This gives a mole fraction of $0.986 < x_{\mathrm{T}} < 0.995$ of *trans*-1,3-butadiene. Therefore, *cis*-1,3-butadiene can be regarded as an impurity with a mole-fraction of $x_{\mathrm{C}} < 0.014$. This leads to a small correction of the measured depolarization ratio $\rho(\nu_0)$ according to

$$\rho_{\mathrm{T}}(\nu_0) \approx \rho(\nu_0) - 135 x_{\mathrm{C}}^{2} \frac{\alpha_{\mathrm{T}}^{2} \Delta\alpha_{\mathrm{C}}^{2} - \alpha_{\mathrm{C}}^{2} \Delta\alpha_{\mathrm{T}}^{2}}{(45\alpha_{\mathrm{T}}^{2} + 4\Delta\alpha_{\mathrm{T}}^{2})^{2}} \qquad (22)$$

where the subscript "T" stands for the trans and "C" for the cis isomer. Although α and $\Delta\alpha$ are to be evaluated at ν_0, we estimate the influence of the impurity *cis*-1,3-butadiene using the calculated data at $\nu_0 = 0$ (see below). The correction to ρ_{T} amounts to less than 0.05% and, therefore, is completely negligible. We conclude that all measured quantities refer to the trans isomer of 1,3-butadiene.

Discussion and Conclusions

The experimental estimate of the static mean dipole polarizability of *trans*-butadiene is $\alpha = 54.64\ e^2a_0^2E_{\mathrm{h}}^{-1}$. This value results from an extrapolation to infinite wavelength of refractivity data obtained by Hohm and Trümper.[12] The present experimental investigation yields for the dipole polarizability anisotropy a value of $\Delta\alpha = 42.5(1.7)\ e^2a_0^2E_{\mathrm{h}}^{-1}$ at 514.5 nm. This value constitutes a useful guide for theoretical efforts. It is now possible to provide a more rigorous analysis of the available theoretical estimates of the dispersion of $\Delta\alpha$.

TABLE 6: Theoretical Predictions and Experimental Predictions for the Dipole Polarizability of *trans*-Butadiene (All Values in Atomic Units)

method	α_{xx}	α_{yy}	α_{zz}	α_{xz}	α	$\Delta\alpha$
			Theory			
CPHF[a]	44.54	36.97	85.72	−7.67	55.74	47.34
CPHF[b]	42.79	32.32	87.77	−9.24	53.26	50.73
TDCHF[c]	43.26	33.34	89.42	−9.79	55.34	54.54
DFT[d]	52.30	37.25	87.86		59.14	
DHF[e]	46.53	37.04	85.84		56.47	
TDHF[f]	45.70	30.00	84.50		53.40	
CCSD[e]	44.40	30.10	71.60		48.70	
TDHF[g]	46.90	36.40	85.50		56.27	
MP2[f]	46.50	36.10	78.50		53.70	
TDHF[h]					52.04	50.29
CCSD[g]					48.79	35.24
EOM-CCSD[g]					49.78	36.26
SCF[i]	48.51	37.78	85.73	−12.26	57.34	48.49
SDQ-MP4[j]	47.84	36.73	76.92	−8.35	53.83	38.75
MP4[k]	48.38	37.27	78.19	−8.02	54.61	39.20
CCSD(T)[l]	47.99	36.89	77.24	−8.22	54.04	38.81
			Experiment			
					54.64[m]	39.5 ± 2.7[n]

[a] Hurst et al.[71] Basis set L at a RHF/6-31G theoretical geometry. [b] Hurst et al.[71] with a 6-31G+ PD basis set. [c] Karna et al.[13] Time-dependent-coupled Hartree−Fock at a theoretical geometry. Basis set 4-31 augmented with diffuse p- and d-GTF on carbon. [d] Matsuzawa and Dixon,[72] at a theoretical geometry. [e] Stout and Dykstra.[73] Derivative Hartree−Fock theory at a model geometry. [f] Norman et al.[14] Basis set 4-31(p,d) at an experimental geometry. [g] Norman et al.[15] Basis set ANO-2 at an experimental geometry. [h] Rozyczko et al.[15] 6-31G augmented with diffuse p- and d-GTF at an experimental geometry. [i] Present investigation. Basis set [5s3p3d1f/3s2p1d]. [j] Present investigation. Basis set [5s3p3d/3s3p]. [k] Present investigation. Basis set [5s3p3d/3s2p]. [l] Present investigation. Basis set [5s3p2d/3s2p]. [m] Hohm and Trümper.[12] Static value, obtained from an extrapolation of refractivity data to infinite wavelength. [n] Static limit estimated from a combination of experimental results (this investigation) and theoretical findings for the dispersion of $\Delta\alpha$. See text.

An inspection of the available static polarizability results reveals that most calculations have been performed with rather small basis sets. Comparisons are rendered even more difficult, since the calculations rarely pertain to a commonly used molecular geometry. We have demonstrated in this work how small differences in the geometrical parameters can lead to substantial changes in the dipole polarizability components. Accordingly, the SCF values of $\alpha/e^2a_0^2E_{\mathrm{h}}^{-1}$ and $\Delta\alpha/e^2a_0^2E_{\mathrm{h}}^{-1}$ reported previously (displayed in Table 6) vary considerably. Hurst et al.[71] obtained 55.74 and 47.34 (basis set L in their paper) and 53.26 and 50.73 (basis set 6-31G+PD) at an RHF/6-31G geometry. Karna et al.[13] employed a 4-31G basis set augmented with diffuse p- and d-GTF on carbon to obtain 55.34 and 54.54. A density functional theory (DFT) calculation by Matsuzawa and Dixon[72] resulted in a mean polarizability value of $\alpha = 59.14$. The derivative Hartree−Fock theory (DHF) calculation by Stout and Dykstra[73] gave $\alpha = 56.47$. The TDHF results by Norman et al.[14] and Rozyczko et al.[15] are obtained with small basis sets and lead to relatively small mean values. Our SCF efforts converge convincingly to the T2 ≡ [5s3p3d1f/3s3p1d] results. Our T2 values are $\alpha = 57.34$ and $\Delta\alpha = 48.49\ e^2a_0^2E_{\mathrm{h}}^{-1}$. The former value is in good agreement with the $\alpha = 56.27$ obtained by Norman et al.[14] with a large (ANO-2 in their work) basis set. The correlated values of Norman et al.[14] and Rozyczko et al.[15] for the mean dipole polarizability are lower than ours. We note again the agreement of the MP2/ANO-2[14] value $\alpha = 53.70$ with our results. The CCSD and EOM-CCSD anisotropy values reported by Rozyczko et al.[15] are lower than ours. Observe that their CCSD $\Delta\alpha = 35.24$, corresponding to

TABLE 7: Full Composition (Exponents and Contraction Coefficients) of the C0 and T0 Basis Sets[a]

substrate			*cis*-butadiene basis set C0			*trans*-butadiene basis set T0		
	carbon				C_1 and C_1'			
S	4232.61	0.002029	D	0.799944	1.0	D	0.794980	1.0
	146.097	0.075411	D	0.107125	1.0	D	0.103550	1.0
	42.4974	0.257121			C_2 and C_2'			
	14.1892	0.596555	D	0.787684	1.0	D	0.784262	1.0
	1.9666	0.242517	D	0.112521	1.0	D	0.110320	1.0
S	5.1477	1.0			H_3 and H_3'			
S	0.4962	1.0	P	1.136363	1.0	P	1.135034	1.0
S	0.1533	1.0	P	0.223213	1.0	P	0.225480	1.0
S	0.0474	1.0			H_4 and H_4'			
P	18.1557	0.018534	P	1.172631	1.0	P	1.168240	1.0
	3.9864	0.115442	P	0.223349	1.0	P	0.227283	1.0
	1.1429	0.386206			H_5 and H_5'			
	0.3594	0.640089	P	1.161291	1.0	P	1.174591	1.0
P	0.1146	1.0	P	0.240990	1.0	P	0.259734	1.0
P	0.0365	1.0						
	hydrogen							
S	19.2406	0.032828						
	2.8992	0.231208						
	0.6534	0.817238						
S	0.1776	1.0						
S	0.0483	1.0						

[a] The sp substrate is common to both basis sets. The carbon and hydrogen atoms are as in Figure 1.

an ECC of 15.05, is 29.9% lower than their TDHF value of 50.29. Our CCSD(T)/T0 results predict a less important ECC for this property.

The experimental estimate of the mean polarizability, $\alpha = 54.64\ e^2a_0{}^2E_h{}^{-1}$, is in very good agreement with our best results, the CCSD(T)/T0 value of 54.04 $e^2a_0{}^2E_h{}^{-1}$. We have neglected the effect of averaging over the ground vibrational state, a rather extraordinary task for a molecule as large as butadiene,[74] but we think that the present agreement is not fortuitous. It is of considerable importance to use the present experimental value of the anisotropy, $\Delta\alpha = 42.5(1.7)\ e^2a_0{}^2E_h{}^{-1}$ at 514.5 nm, to evaluate the theoretical efforts to determine the dispersion of this important property.

A comparison of the dispersion of the dipole polarizability reported by Karna et al.[13] and Norman et al.[14] makes clear that basis set and electron correlation effects may be very important. TDHF methods predict a larger dispersion than all other methods that include electron correlation effects. This is conclusively evidenced by the systematic results reported by Rozyczko et al.,[15] who reported frequency-dependent values obtained at high levels of theory. Their values show that the quantity $\Delta\alpha(514.5\text{ nm}) - \Delta\alpha(0)$ changes from 8.06 (TDHF) to 4.13 (CI-like EOM-CCSD) and 2.55 (quadratic EOM-CCSD) $e^2a_0{}^2E_h{}^{-1}$. They used a rather small basis set, and it seems rather impossible at this stage to deduce a final estimate for the dispersion of $\Delta\alpha$ at 514.5 nm. Accepting the range of values provided by the theoretical efforts, only a very conservative estimate can be advanced for the dispersion of the anisotropy and consequently for the experimental static limit of this important property. For instance, relying on the correlated efforts of Rozyczko et al.,[15] we may deduce an estimate of $\Delta\alpha(514.5\text{ nm}) - \Delta\alpha(0) \approx 3 \pm 1$ and, consequently, a static value of $\Delta\alpha(0) = 39.5(2.7)\ e^2a_0{}^2E_h{}^{-1}$ for *trans*-butadiene. This result represents, as we readily admit, a conservative estimate of the static limit of $\Delta\alpha$. Its agreement with our static result of 38.81 $e^2a_0{}^2E_h{}^{-1}$ should be considered only a slight encouragement. It is now clear that the accurate determination of the dispersion of the dipole polarizability for *trans*-butadiene emerges as a challenge for quantum chemical methods. We hope that the results reported in this work will guide further efforts in the right direction.

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