Experimental Determination of the Anisotropic Electric Dipole Polarizabilities of Molecules of C_s Symmetry: $CH_3CH_2C{\equiv}N$ and $(CH_3)_2CHC{\equiv}N$

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The present report describes the further development of a novel experimental route to the four independent components of the anisotropic electric dipole polarizabilities of molecules of C_s symmetry, originally applied to CH_3NH_2 and $(CH_3)_2NH$ [Ritchie, G. L. D.; Blanch, E. W. *J. Phys. Chem. A* **2003**, *107*, 2093−2099] and here extended to CH_3CH_2CN and $(CH_3)_2CHCN$. Once again, the four equations required to evaluate the four components of the optical-frequency (λ = 632.8 nm) polarizabilities are drawn from observations of (1) the temperature dependence of the electrooptical Kerr effect, (2) the Rayleigh depolarization ratio, and (3) the refractive index of the gas, together with (4) a simple bond-additivity model of the polarizability. Although the measurements are difficult and still much less than routine, the procedure is applicable to many other species of this symmetry, for which free-molecule anisotropic polarizabilities have not previously been experimentally accessible.

Introduction

The electric dipole polarizability, $\alpha_{\alpha\beta}$, is the basic descriptor of the interaction of the molecular charge distribution with an electric field.[1−3] Although the free-molecule polarizability anisotropy of CH_3CN, a species of C_{3v} symmetry, is reliably known,[4] those of its immediate homologues CH_3CH_2CN (ethyl cyanide, propionitrile) and $(CH_3)_2CHCN$ (isopropyl cyanide, isobutyronitrile), both of which have C_s symmetry (and a single plane of symmetry),[5,6] have remained unknown. The reason that this is so is primarily that, in relation to reference axes that are not coincident with the principal axes of the tensor, the polarizability of a species of this symmetry has four independent components ($\alpha_{xx} \neq \alpha_{yy} \neq \alpha_{zz} \neq \alpha_{xy}$) and one of these ($\alpha_{xy}$) is normally much smaller and, at least experimentally, much less accessible than the others. Moreover, the locations of the two in-plane principal axes are not obvious from the molecular structure and they will not necessarily coincide with the principal axes of the moment of inertia or any other molecular property that transforms as a second-order tensor. However, it was shown recently,[7] with CH_3NH_2 and $(CH_3)_2NH$ as examples, that the four components of the polarizability of a species of C_s symmetry can be derived from measurements of (1) the temperature dependence of the electrooptical Kerr constant, (2) the Rayleigh depolarization ratio, and (3) the refractive index, together with (4) a simple bond-additivity model of the polarizability. The study that is reported here focused on the determination of the free-molecule polarizabilities of CH_3CH_2CN and $(CH_3)_2CHCN$, for which the relevant experiments have been conducted. As well, it included, as a preliminary, an analysis of analogous data for CH_3CN and verification that measurements of (1) and, alternatively, (2) yield the same value of the optical-frequency polarizability anisotropy of this species, but because this proved straightforward, from both experimental and theoretical viewpoints, it will not be described in detail here. It would have been of interest, too, to obtain experimental data for $(CH_3)_3CCN$, to complete the sequence CH_3CN, CH_3CH_2CN, $(CH_3)_2CHCN$, $(CH_3)_3CCN$, as was done to advantage with NH_3, CH_3NH_2, $(CH_3)_2NH$, $(CH_3)_3N$. Unfortunately, the diminished volatility and the diminished molecular anisotropy of this compound militated against such measurements. However, in relation to the main objective, reliable values of the anisotropic molecular polarizabilities of CH_3CH_2CN and $(CH_3)_2CHCN$ have been obtained, and the usefulness of the general procedure for species of C_s symmetry has been further demonstrated.

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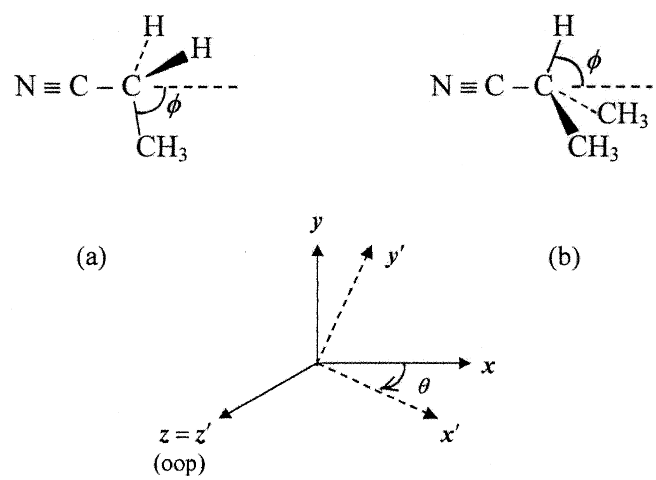

Figure 1. Locations of axes (oop = out-of-plane): *x*, *y*, *z* = reference axes; *x*′, *y*′, *z*′ = principal axes; *x* coincides with the NC−C bond.

Theory

It is necessary, first, to choose convenient reference axes (*x*, *y*, *z*) and, as well, to specify the relationship of these to the principal axes (*x*′, *y*′, *z*′) of the polarizability tensors of CH_3CH_2CN and $(CH_3)_2CHCN$, as shown in Figure 1. The minimum-energy conformations of both molecules have C_s symmetry,[5,6] so only the $z = z'$ (out-of-plane) principal axis, which is perpendicular to the plane of symmetry, is immediately obvious; the locations of the *x*′ and *y*′ principal axes in this plane are not obvious. It is useful to recognize, too, that the reference axes in Figure 1 are judicious choices since, at least in the bond-additivity approximation, the dominant N≡C−C group does not

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contribute to the single off-diagonal component, α_{xy}, of the polarizability. The angles, θ, through which the reference axes x and y must be rotated to locate the principal axes x' and y' can therefore be expected to be small. Note, also, that the directions of action of the dipole moments[5,6] of both CH_3CH_2CN and $(CH_3)_2CHCN$ are such that $\mu_x \neq \mu_y \neq 0$ and $\mu_z = 0$.

In the reference axis system, the polarizabilities of CH_3CH_2CN and $(CH_3)_2CHCN$ have four nonzero components, α_{xx}, α_{yy}, α_{zz}, and α_{xy}, so that the tensors are completely specified by any four independent equations that connect these to physical observables. As recently demonstrated,[7] these can be drawn from measurements of (1) the temperature dependence of the Kerr constant, A_K, (2) the Rayleigh depolarization ratio, ρ_0, and (3) the refractive index or mean polarizability, α, together with (4) a simple bond-additivity model of the polarizability, described in the next section. The model utilizes the known polarizability anisotropy of CH_3CH_3,[4] alone, to estimate the off-diagonal polarizabilities, α_{xy}, of CH_3CH_2CN and $(CH_3)_2CHCN$.

For the axis system defined in Figure 1, the zero-density Kerr constant, A_K, can be formulated as[8]

$$A_K = (N_A/81\epsilon_0)\{\gamma^K + (kT)^{-1}[(2/3)\mu\beta^K + (9/5)\alpha\alpha^0\kappa\kappa^0] + (3/10)(kT)^{-2}[\mu_x^{\,2}(\alpha_{xx} - \alpha) + \mu_y^{\,2}(\alpha_{yy} - \alpha) + 2\mu_x\mu_y\alpha_{xy}]\} \quad (1)$$

in which $\alpha\alpha^0$ ($\approx \alpha^2$) is the product of the mean optical-frequency and static polarizabilities, $\kappa\kappa^0$ ($\approx \kappa^2$) is the product of the optical-frequency and static polarizability anisotropy parameters,[9] β^K and γ^K are the first and second Kerr hyperpolarizabilities,[2] and SI units are implied.[10] Equation 1 has the form

$$A_K = P + QT^{-1} + RT^{-2} \quad (2)$$

or, more conveniently here

$$(A_K - P)T = Q + RT^{-1} \quad (3)$$

where

$$P = (N_A/81\epsilon_0)\gamma^K \quad (4)$$

$$Q = (N_A/81\epsilon_0 k)[(2/3)\mu\beta^K + (9/5)\alpha\alpha^0\kappa\kappa^0] \quad (5)$$

and

$$R = (N_A/81\epsilon_0 k^2)(3/10)[\mu_x^{\,2}(\alpha_{xx} - \alpha) + \mu_y^{\,2}(\alpha_{yy} - \alpha) + 2\mu_x\mu_y\alpha_{xy}] \quad (6)$$

so that, if the left-hand side of eq 3 is plotted against T^{-1} and all other quantities are known, Q gives β^K and R gives the desired equation in the components of the polarizability. The relationship between the Rayleigh depolarization ratio, ρ_0, and the polarizability is

$$5\rho_0(3 - 4\rho_0)^{-1} = \kappa^2 = [(\alpha_{xx} - \alpha_{yy})^2 + (\alpha_{yy} - \alpha_{zz})^2 + (\alpha_{zz} - \alpha_{xx})^2 + 6\alpha_{xy}^{\,2}]/18\alpha^2 \quad (7)$$

where

$$\alpha = (\alpha_{xx} + \alpha_{yy} + \alpha_{zz})/3 \quad (8)$$

is the mean polarizability.[11] The procedure employed here to evaluate the four components of the polarizabilities of CH_3CH_2CN and $(CH_3)_2CHCN$ therefore involves use of the bond additivity model to estimate α_{xy}, followed by simultaneous solution of eq 6−8.

Bond-Additivity Model

The simple bond-additivity model that is invoked here serves two purposes. First, it provides estimates, with what will be seen to be acceptable accuracy, of the small and experimentally inaccessible off-diagonal component, α_{xy}, of the polarizability. Second, it predicts the relative magnitudes of the much larger diagonal components, α_{xx}, α_{yy}, and α_{zz}, and so enables an unambiguous choice to be made between the alternative solutions of the quadratic equation that is involved in the determination of these components from eq 6−8.

In what follows, it is convenient to introduce the irreducible bond-polarizability parameters Γ_{CC} and Γ_{CCN}, defined as

$$\Gamma_{CC} = (\alpha_L^{CC} - \alpha_T^{CC}) - 2(\alpha_L^{CH} - \alpha_T^{CH}) = \gamma^{CC} - 2\gamma^{CH} \quad (9)$$

and

$$\Gamma_{CCN} = (\alpha_L^{CCN} - \alpha_T^{CCN}) - (\alpha_L^{CH} - \alpha_T^{CH}) = \gamma^{CCN} - \gamma^{CH} \quad (10)$$

where α_L and α_T are the longitudinal and transverse polarizabilities of the specified pair or group of atoms. Numerical values of Γ_{CC} and Γ_{CCN} are available from the Rayleigh depolarization ratios and molecular polarizability anisotropies of CH_3CH_3 and CH_3CN,[4] respectively, since, for CH_3CH_3, $\alpha_{zz} - \alpha_{xx} = \Gamma_{CC}$ and, for CH_3CN, $\alpha_{zz} - \alpha_{xx} = \Gamma_{CCN}$. It is also convenient, and does not compromise the purposes detailed above, to assume, in the context of the model, that CH_3CH_2CN and $(CH_3)_2CHCN$ have exactly tetrahedral bond angles, an approximation that greatly simplifies the relevant equations.

In relation to the first objective, and with reference to Figure 1, the off-diagonal polarizabilities of CH_3CH_2CN (a) and $(CH_3)_2CHCN$ (b) emerge as

$$\alpha_{xy}\,(a) = -\{(\alpha_L^{CCH_3} - \alpha_T^{CCH_3}) - 2(\alpha_L^{CH} - \alpha_T^{CH})\cos 60\}\cos\phi\sin\phi \quad (11)$$

and

$$\alpha_{xy}\,(b) = -\{2(\alpha_L^{CCH_3} - \alpha_T^{CCH_3})\cos 60 - (\alpha_L^{CH} - \alpha_T^{CH})\}\cos\phi\sin\phi \quad (12)$$

so that, with $\phi = \arccos(1/3)$ ($= 70.5°$)

$$\alpha_{xy}(a) = \alpha_{xy}(b) = -(2\sqrt{2}/9)\Gamma_{CC} \quad (13)$$

a result that is consistent with the symmetry of these species.

In relation to the second objective, it is sufficient to formulate the three polarizability anisotropies of CH_3CH_2CN and of $(CH_3)_2CHCN$ in terms of Γ_{CC} and Γ_{CCN}, in the knowledge that these quantities are positive in sign and of magnitudes such that $\Gamma_{CC} \approx \Gamma_{CCN}/3$. Now it is straightforward to establish that, for CH_3CH_2CN

$$\alpha_{xx} - \alpha_{yy} = -(7/9)\Gamma_{CC} + \Gamma_{CCN} \quad (14)$$

$$\alpha_{yy} - \alpha_{zz} = (8/9)\Gamma_{CC} \quad (15)$$

$$\alpha_{zz} - \alpha_{xx} = -(1/9)\Gamma_{CC} - \Gamma_{CCN} \quad (16)$$

so that $\alpha_{xx} > \alpha_{yy}$, $\alpha_{yy} > \alpha_{zz}$ and $\alpha_{xx} > \alpha_{yy} > \alpha_{zz}$. For $(CH_3)_2CHCN$

$$\alpha_{xx} - \alpha_{yy} = -(2/9)\Gamma_{CC} + \Gamma_{CCN} \quad (17)$$

$$\alpha_{yy} - \alpha_{zz} = -(8/9)\Gamma_{CC} \quad (18)$$

$$\alpha_{zz} - \alpha_{xx} = (10/9)\Gamma_{CC} - \Gamma_{CCN} \quad (19)$$

so that $\alpha_{xx} > \alpha_{yy}$, $\alpha_{yy} < \alpha_{zz}$, $\alpha_{zz} < \alpha_{xx}$, and $\alpha_{xx} > \alpha_{zz} > \alpha_{yy}$. Of course, the relative magnitudes of α_{xx}, α_{yy}, and α_{zz} could have been predicted simply by inspection of Figure 1, but the bond-additivity model places these results on a firmer basis.

Finally, it must be emphasized that it is not to be expected, and certainly is not claimed here, that the anisotropic polarizabilities (as opposed to the isotropic polarizabilities) of CH_3-CH_2CN and $(CH_3)_2CHCN$ are rigorously additive and therefore accurately predictable from the model. It is, however, claimed that for both molecules α_{xy} is adequately predictable, and that α_{xx}, α_{yy}, and α_{zz} can be reliably placed in order of magnitude, which is all that the procedure requires.

Experimental Section

Samples of CH_3CH_2CN (bp 97.2 °C) and $(CH_3)_2CHCN$ (bp 103.6 °C) were purified by standard methods[12] and subjected to repeated freeze−pump−thaw cycles immediately before use. Because of the relatively high boiling points of these liquids, the experiments were necessarily performed at high temperatures and low pressures.

Apparatus for measurements of the Rayleigh depolarization ratio, $\rho_0 = (I^v_h - I^v_{h,b})/(I^v_v - I^v_{v,b})$, of gases and vapors has been described.[13] Observations on CH_3CH_2CN and $(CH_3)_2CHCN$ were made at 352 K and ≈15−25 kPa. The results are the averages of repeated determinations with inclusion and, indistinguishably, with exclusion by means of an interference filter of vibrational Raman contributions: CH_3CH_2CN, $\rho_0 = (1.040 \pm 0.012) \times 10^{-2}$; $(CH_3)_2CHCN$, $\rho_0 = (0.602 \pm 0.013) \times 10^{-2}$.

Equipment for investigation of the temperature and pressure dependence of the electrooptical Kerr effect in gases and vapors has also been described.[14] Measurements of the electric field-induced birefringences of CH_3CH_2CN and $(CH_3)_2CHCN$ at 632.8 nm were made at 10 temperatures (≈340−500 K) within the available span and, at each temperature, over a range of pressures (≈10−30 kPa). The definition of the molar Kerr constant, ${}_mK$, is[8,15]

$${}_mK = 6nV_m[(n^2 + 2)^2(\epsilon_r + 2)^2]^{-1}[(n_X - n_Y)F_X{}^{-2}]_{F_X=0} \quad (20)$$

where n and ϵ_r are the refractive index and relative permittivity of the vapor in the absence of the field, $n_X - n_Y$ is the birefringence for XZ- and YZ-polarized light that is induced by the uniform electric field, F_X, and V_m is the molar volume. To take account of molecular interactions, ${}_mK$ is expressed in terms of V_m as

$${}_mK = A_K + B_K\, V_m{}^{-1} \quad (21)$$

in which A_K and B_K are the Kerr first and second virial coefficients. In practice, the observed birefringences were used to establish values of

$${}_mK_0 = (2/27)V_m(n_X - n_Y)\, F_X{}^{-2} \quad (22)$$

and these were fitted to the relation[16]

$${}_mK_0 = A_K + [B_K + A_K(2A_\epsilon + (1/2)A_R)]\, V_m{}^{-1} \quad (23)$$

TABLE 1: Temperature Dependence of the Vapor-State Kerr Effects of CH_3CH_2CN and $(CH_3)_2CHCN$ at 632.8 nm

T (K)	no. of pressures	p (kPa)	A_K (10^{-27}m^{5}V^{-2}mol^{-1})
		CH_3CH_2CN	
496.7	6	14−22	175.1 ± 1.2
480.3	8	16−27	189.1 ± 0.3
460.1	8	11−26	203.9 ± 0.7
438.9	8	14−26	224.1 ± 1.1
420.6	7	14−27	244.8 ± 0.3
400.6	7	17−26	269.5 ± 0.5
384.5	8	16−29	291.8 ± 1.0
369.4	9	16−31	317.1 ± 0.6
354.5	8	11−25	345.4 ± 0.7
340.5	7	10−20	377.6 ± 0.9
		$(CH_3)_2CHCN$	
496.6	5	13−27	165.7 ± 0.5
480.3	7	16−29	175.2 ± 0.6
461.0	8	11−29	189.8 ± 0.6
440.7	8	11−28	207.7 ± 0.8
420.5	8	12−27	226.5 ± 0.7
400.7	6	11−26	245.4 ± 0.7
384.5	8	12−25	272.7 ± 0.9
369.4	7	14−27	289.9 ± 0.7
354.5	7	12−24	312.6 ± 0.8
340.6	7	10−17	338.4 ± 1.8

in which A_ϵ and A_R are the low-density molar dielectric polarization and refraction, calculated from the static and optical-frequency molecular polarizabilities. In the absence of density virial coefficients, departures from ideal-gas behavior were assumed to be negligible under the high-temperature/low-pressure conditions of the measurements. The required values of V_m were therefore slightly overestimated, typically by <1% and at worst by <2%. The results are summarized in Table 1, where the errors attributed to the values of A_K are standard deviations from the least-squares fitting of straight lines to the pressure-dependence data; with calibration and other systematic errors the overall accuracy is estimated as ±3%. Values of B_K were poorly determined, because of the limited vapor pressures that were accessible, and are not reported here. Dilute-solution Kerr constants for CH_3CH_2CN and $(CH_3)_2CHCN$ at 298 K have previously been recorded,[17] but local-field effects preclude a direct comparison of gas- and solution-phase data.[18]

Results

In earlier analyses of data for dipolar and anisotropically polarizable species (e.g., CH_3X, CH_2X_2, and CHX_3, X = F, Cl[10,19]), a quadratic equation (eq 2) was reduced to a linear equation (eq 3) by means of an approximation for γ^K, which could be seen to make only a small contribution to A_K under normal conditions. The species of interest here are all the more strongly dipolar, and on the basis of the known value of γ ($\approx \gamma^K$) for CH_3CN,[20] estimated values of γ^K for CH_3CH_2CN ($\gamma^K \approx 2\gamma$) and $(CH_3)_2CHCN$ ($\gamma^K \approx 3\gamma$) contribute only 0.3% and 0.4%, respectively, to the values of A_K at the highest temperatures, so that the same simplification can be made. Figure 2 displays the experimental data and the linear plots of $[A_K - (N_A/81\epsilon_0)\gamma^K]\, T$ against T^{-1}, whereas Table 2 contains the least-squares coefficients Q and R and their interpretation in terms of molecular properties. Although the temperature ranges of the measurements were limited by the involatility of the liquids, values of R, and therefore the derived polarizabilities, were adequately determined.

Other data in Table 2 are values of the depolarization ratio, ρ_0, and the square of the optical-frequency polarizability anisotropy parameter, $\kappa^2 = 5\rho_0(3-4\rho_0)^{-1}$ (eq 7); the mean optical-frequency polarizability, α (eq 8);[21] and the components

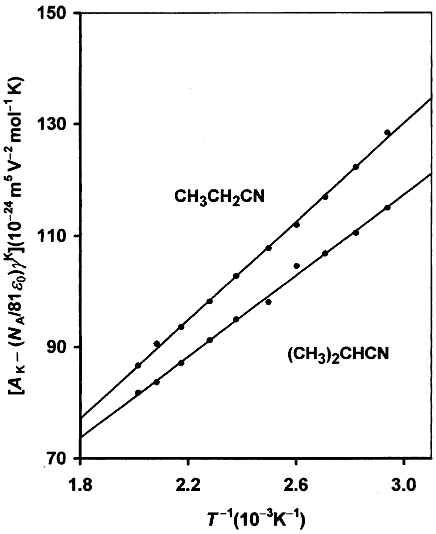

Figure 2. Temperature dependence of A_K of CH_3CH_2CN and $(CH_3)_2$-CHCN.

TABLE 2: Analysis of the Temperature Dependence of A_K of CH_3CH_2CN and $(CH_3)_2CHCN$ at 632.8 nm[a]

property	value	
	CH_3CH_2CN	$(CH_3)_2CHCN$
$P(10^{-27}m^5\ V^{-2}\ mol^{-1})$[b]	(0.5 ± 0.2)	(0.7 ± 0.4)
$Q(10^{-24}\ m^5\ V^{-2}\ mol^{-1}\ K)$[c]	-0.6 ± 1.5	8.8 ± 1.9
$R(10^{-21}\ m^5\ V^{-2}\ mol^{-1}\ K^2)$[d]	43.5 ± 0.6	36.2 ± 0.8
$\rho_0(10^{-2})$	1.040 ± 0.012	0.602 ± 0.013
$\kappa^2(10^{-2})$	1.758 ± 0.020	1.012 ± 0.022
$\alpha\ (10^{-40}C\ m^2\ V^{-1})$[e]	6.93 ± 0.03	8.96 ± 0.04
$\mu(10^{-30}\ C\ m)$	13.51 ± 0.10[f]	14.31 ± 0.33[g]
μ_x	13.47 ± 0.10	14.19 ± 0.33
μ_y	-1.006 ± 0.007	-1.843 ± 0.043
$\alpha_{xy}(10^{-40}\ C\ m^2\ V^{-1})$[h]	-0.25 ± 0.05	-0.25 ± 0.05
α_{xx}	8.71 ± 0.03[i]	10.29 ± 0.04[i]
α_{yy}	6.33 ± 0.20[i]	7.27 ± 0.04[i]
α_{zz}	5.74 ± 0.18[i]	9.33 ± 0.07[i]
$\theta(°)$[j]	6 ± 1	5 ± 1
$\beta^K(10^{-50}\ C\ m^3\ V^{-2})$	-0.3 ± 0.3	1.4 ± 0.3

[a] SI units. Conversion factors for α are $1 \times 10^{-40}\ C\ m^2\ V^{-1} = 6.0651$ au $= 0.89867 \times 10^{-24}$ esu. [b] Equation 4; values estimated from γ ($\approx \gamma^K$) for CH_3CN (ref 20). [c] Equation 5. [d] Equation 6. [e] CH_3CH_2CN: Reference 21a. $(CH_3)_2CHCN$: Calculated as $\alpha = (3\epsilon_0/N_A)_mR$ from molar refraction ($_mR/10^{-6}\ m^3\ mol^{-1}$), interpolated to 632.8 nm (20.32), obtained from data for CH_3CH_2CN and atomic, group and structural refractions in Table 22 of ref 21b. Uncertainties estimated as $\pm$ 0.5%. [f] Reference 5. [g] Reference 6. [h] Bond-additivity model (see text); $\alpha_{xy} = -(2\sqrt{2}/9)\Gamma_{CC}$. [i] Uncertainty is the sum of the contributions that arise form the uncertainties in R and κ^2 (measured standard deviations, given above) and α_{xy} (assumed uncertainty of $\pm$ 20%). [j] Figure 1. $\theta = (1/2)\arctan[2\alpha_{xy}(\alpha_{yy} - \alpha_{xx})^{-1}]$ (see text).

μ_x and μ_y of the electric dipole moment, μ. In relation to the moments of CH_3CH_2CN [5] and $(CH_3)_2CHCN$, [6] Stark-effect measurements have provided the magnitudes but not the signs of the components, so the directions ($-$ to $+$) of the overall moments have remained speculative. However, the ambiguity was easily removed by recourse to a simple bond-additivity model[17] in which the large moment of the $N{\equiv}C{-}C$ group, taken as the moment of CH_3CN, [22] was augmented by one, or two, small induced moments, taken to act along the axis of each polarizable $C{-}CH_3$ group. The molecular moments of CH_3-CH_2CN and $(CH_3)_2CHCN$ are, in fact, inclined at angles of 4.3°[5] and 7.4°, [6] respectively, to the $N{\equiv}C{-}C$ (x) axis (Figure 1) such that, in both cases, μ_x is positive and μ_y is negative in sign. As well, Table 2 includes the value of $\alpha_{xy} = -(2\sqrt{2}/9)\Gamma_{CC}$, calculated from data for CH_3CH_3 in the manner described above; the values of α_{xx}, α_{yy}, and α_{zz}, derived by simultaneous solution of eq 6−8; the angles $\theta = (1/2)\arctan[2\alpha_{xy}(\alpha_{yy} - \alpha_{xx})^{-1}]$,[23] through which the x and y reference axes must be rotated to locate the x' and y' principal axes; and imprecise (and possibly inaccurate) values of the hyperpolarizability, β^K. Note, too, that the analyses in Table 2 confirm that, for both CH_3CH_2CN and $(CH_3)_2CHCN$, A_K is overwhelmingly dominated by the RT^{-2} term. Moreover, for both species the coefficient R is itself similarly dominated by the $\mu_x^2(\alpha_{xx} - \alpha)$ term, with only a small contribution from the $\mu_x\mu_y\alpha_{xy}$ term. Of course, the fact that α_{xy} makes only a small contribution to R (2.0%, 4.7%), and also to κ^2 (2.4%, 2.5%), is the reason that the polarizabilities that emerge for CH_3CH_2CN and $(CH_3)_2CHCN$ are relatively insensitive to the value that is adopted for this parameter.

Discussion

The present report describes the further development of a novel experimental route to the four independent components of the anisotropic electric dipole polarizabilities of molecules of C_s symmetry, originally applied to CH_3NH_2 and $(CH_3)_2NH$ [7] and here extended to CH_3CH_2CN and $(CH_3)_2CHCN$. Unfortunately, the optical (Kerr effect, Rayleigh depolarization, refractive index) and spectroscopic (Stark effect) measurements that are required are still much less than routine but, to date, no other purely experimental procedure has been identified. Nevertheless, the method is clearly applicable to many other simple molecules of this symmetry, for example CH_3CH_2X and $(CH_3)_2CHX$ (X = F, Cl, Br), CH_3XH (X = O, S) and CH_3-COX (X = F, Cl, Br), for which reliable free-molecule polarizabilities are not available. Such studies can be expected to provide valuable information as to the interaction of the molecular charge distributions with electric fields and, eventually, intermolecular forces. As well, the experimental polarizabilities are of much interest in relation to the predictive capability of state-of-the-art computational quantum chemistry.

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(23) For a symmetric second-order tensor such as the polarizability, $\alpha_{\alpha\beta}$, the transformation law is $\alpha_{\alpha'\beta'} = \alpha_{\alpha\beta}a_{\alpha\alpha'}a_{\beta\beta'}$ so that, from Figure 1, $\alpha_{x'y'} = \alpha_{\alpha\beta}a_{\alpha x'}a_{\beta y'} = (1/2)(\alpha_{xx} - \alpha_{yy}) \sin 2\theta + \alpha_{xy} \cos 2\theta = 0$ and $\theta = (1/2) \arctan [2\alpha_{xy}(\alpha_{yy} - \alpha_{xx})^{-1}]$, as required.