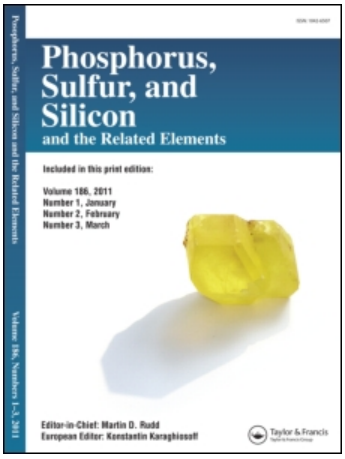

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POLARITY AND POLARIZABILITY PARAMETER DETERMINATIONS IN COMPOUNDS CONTAINING A P-N BOND

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POLARITY AND POLARIZABILITY PARAMETER DETERMINATIONS IN COMPOUNDS CONTAINING A P—N BOND

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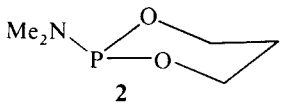
The dipole moments and polarizability ellipsoids of phosphorus-containing bonds in 2,6,7-trimethyl-4-methyl-2,6,7-triaza-1-phosphaicyclo[2.2.2]octane (**3**) and its 1-oxide (**4**) and 1-sulfide (**5**) and in 2-dimethylamino-1,3,2-dioxaphosphorinane (**2**) have been determined from dipole moment, Kerr effect and depolarization of Rayleigh scattering measurements. The conformational rigidity of bicyclic compounds such as (**3**–**5**) as well as of several 2-oxo-2R-4,6-dimethyl-1,3,2-dioxaphosphorinanes are utilized in considering the implications of assuming that the component moments are primarily directed along the phosphoryl bond.

INTRODUCTION

The conformational and electronic properties of organophosphorus molecules become more understandable with a knowledge of moments and polarizability ellipsoids of bonds involving phosphorus. Past efforts in this regard have centered on P—O, P—Cl and P—Ph bonds.[1–3] In the present work we address ourselves to the P—N bond. Although a value for the P—N bond moment m_{P-N} has been determined for $P(NMe_2)_3$ (**1**)[4–6] and for the 1,3,2-dioxaphosphorinane **2**[7] both of which are conformationally mobile, we here



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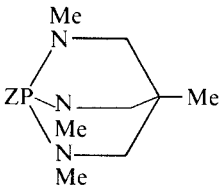
determine m_{P-N} with greater precision for the rigid bicyclic molecule **3** and comment on its opposite direction to that in **1** and **2**.



3 Z = l_P
4 Z = O
5 Z = S

An analysis is put forward herein for the constancy of $m_{P=O}$ from $OP(NMe_2)_3$ to **4** and the lack thereof from $OP(OR)_3$ to its bicyclic analogue $OP(OCH_2)_3CMe$. The vectorial addition of component moments in some rigid highly polar 2-oxo-1,3,2-dioxaphosphorinanes is seen to be compatible with literature values for phosphoryl compounds which are represented by the component moments, in cases where steric interactions are not important.

The principal polarizabilities of **3**–**5** are calculated and a value for the polarizability anisotropy of the P—N bond γ_{P-N} is obtained. The latter value is then broken down into its longitudinal and transverse components. From the Kerr constants of **4** and **5** and γ_{P-N} for **3**, $\gamma_{P=O}$ and $\gamma_{P=S}$ values are calculated and are separated into their longitudinal and transverse components for **4** and **5**. Finally, values of γ_{P-N} and γ_{P-O} are also obtained for **2** and compared with γ_{P-N} obtained for **3** and with γ_{P-O} determined earlier for a related 1,3,2-dioxaphosphorinane.[1]

RESULTS AND DISCUSSION

Dipole Moment of **3**

The bicyclic molecules **3**–**5** possess a three-fold symmetry axis and the polarizability of these cages is described by an ellipsoid in which one

axis ($b_{\parallel}$) coincides with the symmetry axis and the molecular dipole direction. The other two ellipsoidal axes are equal to one another ($b_{\perp}$). From measurements of the total polarization (P_{∞}), the molecular refraction (MR_D), the molecular anisotropy (γ^2) and the molar Kerr Constant ($_mK$), the dipole moments of molecules having axially symmetrical polarizability ellipsoids can be calculated using the formula of Vul'fson and Vereschchagin:[8]

$$\mu^2 = 0.9763 \times 10^{-16} \times T\left(1.4776 \times 10^{-38}\,{}_mKT - \frac{P_E + P_A}{P_E}\gamma^2\right)(\pm(\gamma^2)^{-1/2}) \quad (1)$$

where

$$P_A = P_E \times \left[\frac{1.48 \times 10^{-38}\,{}_mKT \pm 1.682 \times 10^{-24} P_{\infty}\sqrt{\gamma^2}}{\gamma^2 \pm 1.682 \times 10^{-24} P_E \sqrt{\gamma^2}} - 1\right] \quad (2)$$

In Eqs. (1) and (2), T is the absolute temperature, P_E is the electronic polarization, P_A is the atomic polarization and N_A is Avogadro's number. The molecular anisotropy γ^2 can be calculated from Eq. (3):

$$\gamma^2 = {}_{\infty}\delta_2^2\left(\frac{2.1375 MR_D}{\pi N_A}\right)^2 \quad (3)$$

where ${}_{\infty}\delta_2^2$ is the measured solute molecular polarizability anisotropy.

Assuming that to a reasonable approximation $P_E = 0.95\ MR_D$ for 3 and calculating the values of $P_{2\infty}$ by the Halverstad–Kumler equation[9]

$$P_{2\infty} = \frac{3\alpha_1 M_2}{(\varepsilon_1 + 2)^2} + M_2(\nu_1 + \beta)\frac{(\varepsilon_1 - 1)}{(\varepsilon_1 + 2)} = 119\ \text{cm}^3 \quad (4)$$

then the measured values of MR_D, ${}_mK$ and ${}_{\infty}\delta_2^2$ for **3** can be used to calculate P_A from Eq. (2). The value of 6.99 cm^3 for P_A is related to P_E by

$$P_A = 13\%\ P_E \quad (5)$$

Relationship 5 differs only slightly from the usual assumption that $P_A = 10\%\ P_E$.[10] Substituting $P_A = 6.99\ cm^3$ into Eq. (1) gives $\mu = 1.73$ D which is to be compared with $\mu = 1.79$ D obtained from the Guggenheim–Smith equation[1] wherein a contribution from P_A (see Experimental section) is present.

N—P Bond Moments

From the dipole moment of **3** obtained from Eq. (1), the geometrical parameters of **4**,[12] and the assumptions which follow, it becomes possible to calculate an NP bond moment (m_{NP}) for **3**. For the purposes of this calculation it is assumed that $m_{H\to C} = 0.28$ D,[6,7] $m_{C\to N} = 0.53$ D,[6,7] and $\widehat{NPN} = 96.5(\pm 1.0)°$ as in **1**.[13] The $\widehat{NPN}$ angle in **3** should be considerably smaller than in **4** (103.2°)[12] owing to the lower oxidation state of phosphorus in **3**. The further assumption is made that only the phosphorus atom in **3** is moved along the C_3 axis away from the nitrogens (relative to its position in **4**) in order to accommodate the oxidation change. Thus only the angles involving phosphorus are changed as shown in Figure 1.

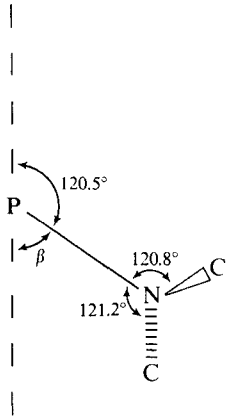


FIGURE 1 Schematic configuration of a portion of **3** showing the bond angle changes from those in **4**.

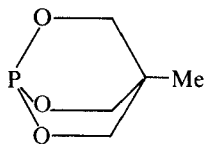
The quantity m_{NP} for **3** can be expressed as

$$m_{NP} = \frac{\mu - 3m_{H\to C} - 3m_{C\to N}^{endo}\cos\eta^{endo} + 3m_{H_3C\to N}^{exo}\cos\eta^{exo}}{3\cos\beta} \quad (6)$$

where the resultant of all the H → C bond moment vectors (except those associated with the exocyclic H → C bond moments) is taken to be equivalent to three H → C moments directed along the C_3 axis towards phosphorus (0.84 D). In Eq. (6) η^{exo} is the dihedral angle between the exocyclic C—N bond and the C_3 axis and η^{endo}

refers to a similar dihedral angle between the endocyclic C—N bond and the C_3 axis. Average values for the η^{exo} (64.5°) and η^{endo} (1.5°) can be calculated from the atom positions and cell parameters for **4**[12] giving a value of 0.23 ± 0.04 D for $m_{N\rightarrow P}$. The uncertainty in this value was calculated as shown in the Appendix.

The N—P bond moment having the direction N → P determined above for **3** (0.23 ± 0.4 D), can be compared with those of **1** (0.31 D)[6] and **2** (0.37 D)[7] which have been calculated to be in the opposite direction, i.e., from P → N. The value for **1** was based on the gas phase structure deduced from electron diffraction data.[13] The uncertainty of ±0.22 D in this value as analyzed in the Appendix is quite large, however. It does appear reasonable to conclude that the P—N bond moment for **3** is in a direction (N→P) opposite to that expected on electronegativity grounds. A similar conclusion was reached for the PO_3 and PS_3 group moments in **6** and **7**, respectively, on the basis of solution dipole moment measurements.[3]



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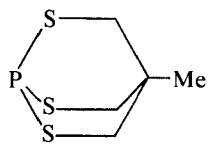

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In compound **1** (and probably **2**) it would appear that the lack of geometrical constraint permits the P—N bond moment to assume the expected P → N direction, although it could be very near 0 D considering the uncertainty in the calculated value (0.31 ± 0.22 D). It should be pointed out that Nifant'ev *et al.*[5] have given a formula for m_{PN} of **1** which is based on the conformation in which a methyl carbon from each nitrogen is co-parallel with the C_3 axis. The formula, however, employs the angles determined from the electron diffraction study[13] and the solution dipole moment of 1.24 D[5] to give $m_{P\rightarrow N}$ = 0.15 D. Furthermore, assuming a model with free rotation about the P—N bonds,[14] we calculate $m_{P\rightarrow N}$ = 0.12 D using the angle determined by Vilkov.[13] While these values appear to be consistent with an expectation of a P→N direction for the P—N bond moment, it should be noted that if the dihedral angle ϕ between the CNC bisector and the NPN bisector is allowed to change from the 60° found in the gas phase structure to 109°, the recalculated P—N bond moment for **1** is the same in magnitude and direction as that calculated above for the cage compound **3**.[15] Thus in view of the large variations in P—N bond moments with conformational changes (*ca.* 0.5 D in the present case), it is clear that a foreknowledge of the precise solution conformational properties of such non-rigid molecules is necessary if solution measurements are to be used to derive these moments. A similar sensitivity to substituent conformation has been noted for P=O and P=S bonds in the corresponding 2-oxo and 2-thio-1,3,2-dioxaphosphorinanes (*ca.* 0.3 D).[1,16]

TABLE I

Experimental results for compounds **2**–**5**

Compounds	Solvent	μ	${}_mK10^{12}$	${}_\infty\delta_2^2 10^3$	MR_D
2	C_6H_{12}	1.72	30.5	4.7	35.15[a]
3	C_6H_{12}	1.73[b]	−71	2.7	53.97
		1.79[c]			
	CCl_4	1.62[d]			
4	CCl_4	5.0	103	—	52.72
	MeC_6H_5	3.77[e]			
	C_6H_{12}	4.33[e]			
5	CCl_4	4.92	658.5	—	60.47

[a] Measured for liquid **2**.

[b] Calculated by means of the Vul'fson–Vereshchagin formula (see text).

[c] Calculated by means of the Guggenheim–Smith equation (see text).

[d] R. D. Bertrand, R. D. Compton, and J. G. Verkade, *J. Chem. Soc.*, **92**, 2702 (1970).

[e] Ref. 27.

TABLE II

Dipole moments and polarizability anisotropies of P=X bonds in YP=X compounds

	X = O				X = S			
Y	$m_{P=O}$ (D)	b_L (Å^3)	γ (Å^3)	Ref.	$m_{P=S}$ (D)	b_L (Å^3)	γ (Å^3)	Ref.
$MeC(CH_2NMe)_3$	3.27	3.36	2.60	this work	3.19	7.66	4.68	this work
	2.71			27				
	2.10			27				
$MeC(CH_2O)_3$	2.95[a]	2.19	0.81	30	2.62[a]	6.72	3.26	30
	3.16			3				
	3.03			—[b]				
$(Me_2N)_3$	2.43			27				
	2.81			—[c]				
	2.74			—[d]				
	3.00			23	3.00			23
$(RO)_3$[e]	0.87–1.19			26	0.98–1.15			23, 26
$(PhO)_3$	1.52			—[b]				
Ph_3	2.91			26	3.35			—[b,f]
	2.95			13	3.3			13
	3.00			23	3.39			23
Me_3	3.40	2.0	0.5	13	3.88	7.0	3.1	13
	3.10			23	3.54			23
R_3[g]	2.90			—[g]				
F_3	2.80			26	1.66			26
	2.76			23				
Cl_3	3.13	2.54	1.52	13	2.03	7.88	5.16	13
	2.98			23	2.32			26
	3.31			26	1.98			23

[a] T. L. Brown, J. G. Verkade, and T. S. Piper, *J. Phys. Chem.*, **65**, 2051 (1961).
[b] C. W. N. Cumper and A. P. Thurston, *J. Chem. Soc. B*, 422 (1971).
[c] D. Bessere and M. Troquet, *Bull. Soc. Chim., Fr.*, 855 (1974).
[d] J. Fayet, *C. R. Acad. Sci.*, **270**, 9 (1970).
[e] R = Me, Et, *n*-Pr, *i*-Pr and *n*-Bu.
[f] I. P. Romm, E. N. Guryanova, N. A. Rozavelskaya and K. Kocheshkov, *Tetrahedron Lett.*, 33 (1977).
[g] C. W. N. Cumper, A. A. Foxton, J. Read, and A. I. Vogel, *J. Chem. Soc.*, 430 (1964). The $m_{P=O}$ value reported is precise to three significant figures (2.87_5) for R = Et, *n*-Pr, *n*-Bu and *n*-Pent.

The $m_{P=O}$ and $m_{P=S}$ bond moment ranges assembled in Table II were calculated for a variety of compounds by taking differences of the measured moments of the phosphoryl and thiophosphoryl derivatives and those of the corresponding trivalent phosphorus parent molecules. The $m_{P=O}$ values are rather constant at about 3.0 D. Pertinent to the present work is the relative constancy of $m_{P=O}$ between acyclic $OP(NMe_2)_3$ and the cage analog **4**. In the latter compound, no significant change in $m_{P=O}$ is expected since the m_{C-N} vectors of each Me_2N group are resolved along the corresponding N—P bond owing to the essentially trigonally planar nitrogen in these systems. Although phosphorus substituents such as R, Ar and NR_2, have conformational flexibility, there is comparatively little influence of this effect on the molecular moment. Examination of the data for thiophosphoryl compounds in Table II reveals a similar situation for these derivatives. As has been noted previously,[17] $m_{P=S}$ values are more sensitive to changes in electronegativity of the phosphorus substituents, leading to the trend $R_3 \cong Ar_3 > N_3 > MeC(CH_2O)_3 > Cl > F$. Note that $m_{P=S}$ for the $MeC(CH_2O)_3PS$ molecule is used in defining this trend since the alkoxy moiety does not change conformation from the parent $MeC(CH_2O)_3P$ molecule from which this bond is calculated.

Principal Polarizabilities of **3–5** *and the Polarizability Anisotropies of Phosphorus Bonds*

The C_{3v} symmetry of **3–5** permits calculation of the principal polarizabilities $b_\parallel$ and $b_\perp$ from Eqs. 7–9:[8]

$$MR_\infty = P_E = \tfrac{4}{9}\pi N_A(b_\parallel + 2b_\perp) = 0.95\ MR_D \quad (7)$$

$$\gamma^2 = 2(b_\parallel - b_\perp)^2 \quad (8)$$

$$m^K = \frac{2\pi N_A}{9}(\theta_1 + \theta_2) \quad (9)$$

$$\theta_1 = \frac{1}{45kT}\left[\frac{P_E + P_A}{P_E}\,2(b_\parallel - b_\perp)^2\right] \quad (10)$$

$$\theta_2 = \frac{1}{45k^2T^2}\,\mu^2 2(b_\parallel - b_\perp) \quad (11)$$

The values of θ_1 and θ_2 can be determined from the experimental values of ${}_\infty\delta_2^2$, ${}_mK$ and μ^2. The values of θ_1 and θ_2 are 0.617×10^{-35} and -17.517×10^{-35}, respectively. The principal semi-axes $b_\parallel$ and $b_\perp$ of the molecular polarizability ellipsoids obtained from these values of θ_1 and θ_2 are 18.84 Å^3 and 21.07 Å^3, respectively, for **3**, 20.10 Å^3 and 19.73 Å^3, respectively, for **4** and 24.40 Å^3 and 21.95 Å^3, respectively, for **5**.

From a knowledge of $b_\parallel$, $b_\perp$, ${}_\infty\delta_2^2$ and ${}_mK$ for **3**, the polarizability anisotropy of the P—N bond, γ_{P-N} can be calculated by a procedure discussed elsewhere.[18] Thus $\gamma_{P-N} = 2.81$ Å^3 when the values b_L(C—N) = 0.57 Å^3, b_T(C—N) = 0.69 Å^3 and b_L(C—H) = b_T(C—H) = b_V(C—H) = 0.64 Å^3 [18] are employed. Since γ_{P-N} is the difference in the longitudinal and transverse polarizabilities

$$\gamma_{P-N} = b_L(P—N) - b_T(P—N) \quad (12)$$

and the total polarizability is expressed by

$$b_{P-N} = \tfrac{1}{3}(b_L + 2b_T) \quad (13)$$

then $b_L = 3.04$ Å^3 and $b_T = 0.23$ Å^3 when b_{P-N} is assigned[19] a value of 3.50 Å^3.

Tensor expansion of the Kerr constants of **4** and **5** using the above γ_{P-N} value for **3** yields $\gamma_{P=O} = 2.60$ Å^3, b_L(P=O) = 3.36 Å^3 and b_T(P=O) = 0.76 Å^3 for the phosphoryl linkage and $\gamma_{P=S} = 4.68$ Å^3, b_L(P=S) = 7.66 Å^3 and b_T(P=S) = 2.98 Å^3 for the thiophosphoryl bond. The γ values obtained in this calculation differ considerably from those obtained by Aroney and LeFevre for $OP(OCH_2)_3CMe$ ($\gamma_{P=O} = 0.81$ Å^3) and $SP(OCH_2)_3CMe$($\gamma_{P=S} = 3.46$ Å^3).[20] The lack of structural data at the time of their work on the latter compounds may play a role in this discrepancy, however.

A similar procedure was used to determine the polarizability ellipsoid of the P—N bond in **2**. Here, however, the phosphorus environment is not symmetrical and so the Kerr constant and molecular anisotropy were each considered to be a function of the two unknowns $\gamma_{P-N}(\gamma')$ and $\gamma_{P-O}(\gamma)$. A chair form for the ring was assumed[7] and two rotational positions of the Me_2N group were considered: one in which the nitrogen and phosphorus lone pairs are parallel (dihedral angle $y = 0°$) and one in which they are perpendicular to one another, ($y = 90°$). For $y = 0°$

$$\theta_1 \times 10^{35} = 1.1651 + 1.5818\gamma + 2.1424\gamma^2 - 0.34\gamma' - 3.7016\gamma\gamma' + 1.9988(\gamma')^2 \quad (14)$$

and

$$\theta_2 \times 10^{35} = 2.8808 - 2.6066\gamma + 4.1\ 449\gamma' \quad (15)$$

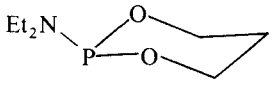
while for $y = 90°$

$$\theta_1 \times 10^{35} = 1.7414 + 2.6190\gamma + 2.1424\gamma^2 - 1.1395\gamma' - 3.7017\gamma\gamma' + 1.9988(\gamma')^2 \quad (16)$$

and

$$\theta_2 \times 10^{35} = 2.2550 - 2.6066\gamma + 4.1449\gamma' \quad (17)$$

From the experimental data in Table I, $\theta_1 = 0.3973$ and $\theta_2 = 6.8461$. In deriving these equations dipole moment components along the coordinate axes were used which were calculated from a comparison of the dipole moments of **8** and **9** wherein an equatorial disposition of the NEt_2 groups is assumed[7] and $m_{P=O} = 0.65$ D and $m_{P=N} = 0.37$ D were employed.



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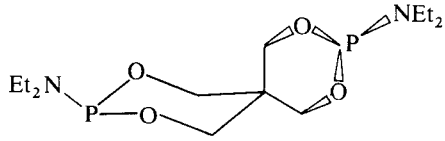

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By solving the pairs of equations for $y = 0°$, $\gamma = \gamma_{P-N} = -3.70$ Å or 2.57 Å^3 and $\gamma' = \gamma_{P-O} = -1.76$ Å^3 or 2.18 Å. Similarly for $y = 90°$, $\gamma = \gamma_{P-N} = -3.98$ Å^3 or 2.24 Å^3 and $\gamma' = \gamma_{P-O} = -2.24$ Å^3 or 2.12 Å^3. The solutions which are high and negative are considered unrealistic. The positive solutions are more reasonable in magnitude and those for γ_{P-O} are in good agreement with the value previously obtained for other 1,3,2-dioxaphosphorinanes.[1] Because the anisotropy of the C—N bond is relatively small, the acceptable solutions for $y = 0°$ and $y = 90°$ are not very dif-

ferent and a choice is difficult. The solutions for the perpendicular lone pair conformation may be preferred, however, since there is strong evidence for this conformation both in acyclic systems[21,22,23] as well as in the solid state structures of phosphorinanes such as **6**, **7** and **8**.[21,24,25] For γ_{P-O} = 2.24 Å^3, b_L(P—O) = 2.74 Å^3, $\bar{b}_T$(P—O) = 0.50 Å^3 and the average polarizability $\bar{b}$ = 1.25 Å^3. For γ_{P-N} = 2.12 Å^3, b_L(P—N) = 2.58 Å^3, b_T(P—N) = 0.46 Å^3 and $\bar{b}$ = 1.17 Å^3. The data for the P—N bond are in good agreement with the polarizability anisotropy calculated for the bicyclic analog **3**, from which a constancy of this parameter from $P(OR)_2NR_2$ compounds to $P(NR_2)_3$ systems can be inferred. These data may therefore be useful in investigations of other organophosphorus molecules which contain the P—N link.

EXPERIMENTAL

Preparations for **3**–**5** have been described previously.[26] Compound **2** was prepared by reacting twice the stoichiometric amount of dimethylamine with $ClP(OCH_2)_2O$[4] in ether. After filtration of the Me_2NH_2Cl, distillation of the filtrate yielded **2** in 50% yield (bp 73–75°/10 mm; n_D^{25} = 1.4695; Anal. Calcd. for $C_5H_{12}NO_2P$: C 40.27, H 8.11, P 20.77; Found: C 39.97, H 8.26, P 20.57).

Dipole moments (μ) molar Kerr Constants ($_mK = {}_{\infty m}K_2$) molecular polarizability anisotropies ($_\infty\delta_2^2$) and molecular refractions (MR_D) were determined from experimental data using standard procedures[18,27] by means of the equations

$$\mu = \sqrt{\frac{9kT}{4\pi N_A}}\,P_0$$

$${}_\infty(P_0)_2 = \frac{M_2}{d_1}\left[\frac{3\alpha\varepsilon_1}{(\varepsilon_1+2)^2} - \frac{3\gamma' n_1^2}{(n_1^2+2)^2}\right]$$

$${}_mK = {}_{\infty m}K_2 = M_2[{}_sK_1(1 - B + \gamma + \delta - H_1\gamma - J_1\alpha\varepsilon_1)]$$

$${}_\infty\delta_2^2 = \delta_1^2\left(1 + A + D + \frac{M_1 - M_2}{M_1} + \frac{7A\Delta_1}{6 - 7\Delta_1}\right)$$

$$MR_D = \frac{M_2}{d_2}\frac{(n_2^2 - 1)}{(n_2^2 + 2)}$$

where k = the Boltzmann constant, T is the absolute temperature, N_A is Avogadro's number, M is the molecular weight, ε is the dielectric constant, n is the index of refraction, d is the density, ${}_\infty(P_0)_2$ is the orientation polarization of the solute, B is the double birefringence, Δ is the Rayleigh scattering depolarization factor, H_1 and J_1 are coefficients, ${}_sK_1$ is the specific Kerr constant of the solvent, δ_1^2 is the nominal coefficient of the depolarization of the Rayleigh scattering of light by the solvent and the subscripts 1, 2 and 12 refer to solvent, solute and solution, respectively. The following relationships hold and the quantities on the left side of the equations are considered to be linearly dependent on weight (W_2) or molar (f_2) concentrations as W_2 or f_2 approach zero.[18]

$$\varepsilon_{12} = \varepsilon_1(1 + \alpha W_2) \qquad d_{12} = d_1(1 + \beta W_2)$$

$$n_{12} = n_1(1 + \gamma W_2) \qquad d_{12} = d_1(1 + Df_2)$$

$$n_{12}^2 = n_1^2(1 + \gamma' W_2) \qquad B_{12} = B_1(1 + \delta W_2)$$

$$\Delta_{12} = \Delta_1(1 + Af_2)$$

All measurements were made at 25°C and the wavelength of light used was λ = 5893 Å. Constants for the solvents used are given in Table III. Electric double birefringences were measured on an instrument similar to that described by LeFevre,[18] refractive indices were obtained on a Pulfrich refractometer and densities were measured with a pycnometer. Dielectric constants and Rayleigh scattering depolarization factors were determined by methods described earlier.[2,28]

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TABLE III

Constants of solvents used

Solvent	E_1	d_1	n_1	$B_1 10^7$	${}_sK \times 10^{14}$	H	J	Δ_1	$\delta_1^2 \times 10^3$
CCl_4	2.227	1.5845	1.4575	0.07	0.749	2.06	0.473	0.04	1.312
C_6H_{12}	2.0199	0.7739	1.4235	0.059	1.460	2.013	0.498	0.06	2.592

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15. In this calculation $m_{C\rightarrow N}$ was assumed to be 0.53 D as before. It may be noted that since changes in molecular conformation affect m_{P-N}, $m_{C\rightarrow N}$ will also be influenced as well. The importance of this influence is difficult to assess, however.
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Appendix

The uncertainty in $m_{N\rightarrow P}$ for **3** was calculated using the equation below which can be derived from Eq. (6) in the text:

$$|\Delta m_{N\rightarrow P}| = |m_{N\rightarrow P}|\left[\frac{|\Delta\mu| + |3m^{endo}_{C\rightarrow N}\Delta\cos\eta^{endo}| + |3m^{exo}_{H_3C\rightarrow N}\Delta\cos^{exo}|}{|\mu - 3m_{H\rightarrow C} - 3m^{endo}_{C\rightarrow N}\cos\eta^{endo} + 3m^{eno}_{H_3C\rightarrow N}\cos^{exo}|} + \left|\frac{3\Delta\cos\beta}{\cos\beta}\right|\right]$$

where

$$\frac{3\Delta\cos\beta}{\cos\beta} = \frac{\Delta\cos\widehat{NPN}}{1 + 2\cos\widehat{NPN}}$$

and

$$|\Delta\cos\eta| = |\sin\eta||\Delta\eta|$$

where η is in radians.

The error in $m_{P\rightarrow N}$ for **1** was calculated using the equation

$$|\Delta m_{P\rightarrow N}| = \left[\left|\frac{\Delta\mu}{\mu}\right| + \left|\frac{\Delta\cos\rho}{1+\cos\rho}\right|\right]\left|\frac{\mu}{\sqrt{3+\cos\rho}}\right| + 2|m_{H_3C\rightarrow N}|\left\{|\Delta\cos\varepsilon| + \left[\left|\frac{\Delta\cos\phi}{\cos}\right| + \frac{\left|\Delta\cos\frac{\delta}{2}\cos\frac{\delta}{2}\right| + |\Delta\cos\varepsilon\cos\varepsilon|}{\left|\cos^2\left(\frac{\delta}{2}\right) - \cos^2\varepsilon\right|} + \frac{3|\Delta\cos\rho|}{|(2-2\cos\rho)||(1+2\cos\rho)|}\right]\right.$$
$$\left.\times\left|\cos\phi\left(\cos^2\left(\frac{\delta}{2}\right) - \cos^2\varepsilon\right)^{1/2}\left[\frac{2-2\cos\rho}{1+2\cos\rho}\right]^{1/2}\right|\right\}$$

which was derived from the formula

$$m_{P\to N} = \frac{\mu}{\sqrt{3}(1 + 2\cos\rho)^{1/2}} - 2m_{H_3C\to N}\left[-\cos\varepsilon + \cos\phi\left(\cos^2\left(\frac{\delta}{2}\right) - \cos^2\varepsilon\right)^{1/2}\left(\frac{2 - 2\cos\rho}{1 + 2\cos\rho}\right)^{1/2}\right]$$

where the angles NPN = $91.5 \pm 1° = \rho$, $\widehat{PNC} = 119.5 \pm 1.5° = \varepsilon$, $\widehat{CNC} = 113.5 \pm 1.5° = \delta$ and the angle ϕ formed between the bisector of $\widehat{CNC}$ and the bisector of NPN = 60°.