of phosphorus oxychloride. To this magnetically stirred mixture at ambient temperature was added portionwise, over approximately 15 minutes, with caution (exotherm!) 41.6 grams (0.2 mole) of phosphorus pentachloride. Homogeneity occurred when approximately two-thirds of the phosphorus pentachloride was added. The resulting dark amber solution was stirred for one day at room temperature—one-hour reflux led only to decomposition products. It was poured onto an excess (ca. 2 kg.) of ice, stirred efficiently to decompose phosphorus oxychloride and phosphorus pentachloride, and extracted with benzene until the benzene extracts were nearly colorless. The benzene extract was washed successively with cold dilute sodium hydroxide and water, dried (anhydrous calcium chloride), and filtered. Concentration of the filtrate left an orange oil which crystallized on standing. This solid was dissolved in a small amount of hot hexane and filtered from a small amount of hexane-insoluble material. Chilling of the filtrate deposited 23 grams (85%) of yellow-orange crystals, m.p. 66.5–68° C., [lit. (*5*), m.p. 69° C.].

A small amount (ca. 4 to 6 grams) of starting material (identified by superimposable infrared spectra) precipitated, on acidification of the combined sodium hydroxide wash, with the original aqueous extract.

Chromatography of 5-Dimethylamino-1-naphthalenesulfonyl Chloride. Ultraviolet light visualization of thin-layer chromatographed dansyl chloride (hexane recrystallized) showed a blue fluorescent spot near the origin of the chromatogram, due to small amounts of unreacted 5-dimethylamino-1-naphthalenesulfonic acid. Chromatographically pure dansyl chloride [one spot, R_f 0.62, R_f (methyl yellow) 0.52; dichloromethane] was obtained by column adsorption chromatography on silica gel, or preferably on alumina.

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Dielectric Constants, Dipole Moments, and Molecular Structure of Some Bicyclic Nitriles and Aliphatic Dinitriles

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Dielectric constants of a series of bicyclic nitriles and aliphatic dinitriles were measured as a function of temperature. Within each series, a number of compounds had a molecular configuration allowing them to exhibit rotational freedom well below their freezing point. Dipole moments for the bicyclic nitriles and aliphatic dinitriles were determined according to the method of Halverstadt and Kumler and compared with dipole moments calculated using the Onsager equation. Differences between the observed and calculated moments are explained in terms of dipolar-dipolar interaction, suggesting the possibility of several modes of association in organic nitriles.

POLAR organic materials that have a high dielectric constant in the liquid state usually have a low dielectric constant when solid, because as the material solidifies, the dipoles become frozen in, and the molecules can no longer orient with the electric field. However, a number of organic materials do not follow this general pattern of dielectric behavior. These materials, called solid rotators, retain their freedom of rotation in the solid state because their molecules approach a spherical shape and there is sufficient free volume so that there is little interference to dipolar orientation and they therefore have a high dielectric constant well below their melting points.

The literature dealing with solid rotators has been reviewed by Smyth (*17, 19*). Nearly all of the rotators discussed by Smyth have small rotational radii. However, camphor and a few other related bicyclic compounds with molecules of rather complicated but nearly spherical structure were also found to be solid rotators. We felt that systematic study of some structurally related rotators would give useful information to help explain the dielectric behavior of these materials.

Several bicyclic nitriles, having the same basic bicyclo[2,2,1]heptane skeleton as camphor, which were prepared in our laboratory (*16*), were found to have a physical property of "plastic crystallinity" usually associated with rotators (*19*). This observation sparked our interest to investigate the dielectric behavior of a group of related bicyclic nitriles, because the presence of a cyano group is known to result in very strong dipole-dipole interactions (*6*), manifested by a high degree of intermolecular association, which *a priori* would seem incompatible with the

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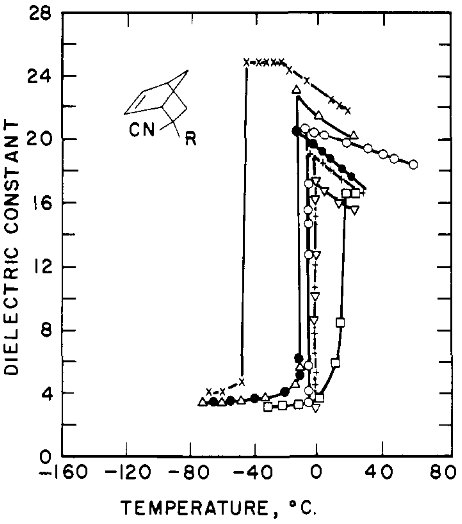


Figure 1. Dielectric constant as a function of temperature for a series of exo-alkyl *endo*-cyanonorbornenes

Sym	R	M.P., ° C
X	H	23–24
O	CH_3	46–47
Δ	CH_2CH_3	−6—8
●	C_3H_7	−15—16
+	C_4H_9	5
□	i-C_4H_9	15
▽	C_5H_{11}	−2

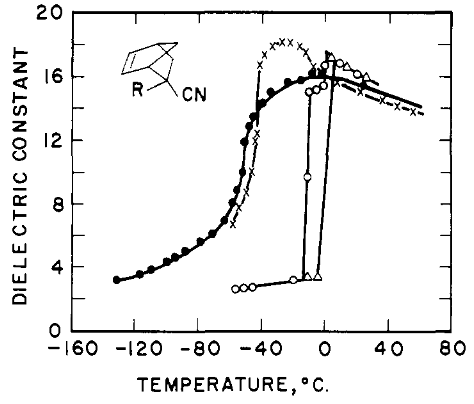


Figure 2. Dielectric constant as a function of temperature for a series of *endo*-alkyl exo-cyanonorbornenes

Sym	R	M.P., ° C
O	H	8
X	CH_3	63–64
Δ	CH_2CH_3	9.5–12
●	CH_3	63–64
●	Disk sample	

requirement that the individual molecules rotate freely in the solid state.

This paper presents the results of the study of the electrical behavior of a number of bicyclic nitriles, and of a parallel study of the electrical behavior of a group of spherical aliphatic dinitriles and their interpretation in terms of molecular structure and dipolar interactions.

EXPERIMENTAL

Materials. 2-*exo*-cyano-5-norbornene (*1*), 2-*endo*-cyano-5-norbornene (*1*), 2-*exo*-cyano-2-*endo*-methyl-5-norbornene (*16*), 2-*exo*-cyano-2-*endo*-ethyl-5-norbornene (*16*), and 2-cyanobicyclooctane (*1*) were prepared according to previously described procedures. The 2-*exo*-alkyl-2-*endo*-cyano-5-norbornenes were prepared by the method of Boehme *et al.* (*4*), and are listed in Table I with their physical properties. (All new compounds were prepared by well established procedures. Satisfactory elemental analyses and infrared spectra were obtained for all new compounds.) 2,2-Dicyanonorbornane (m.p. 95° C) was prepared via the Diels-Alder adduct of ethyl cyanoacrylate and cyclopentadiene, which was hydrogenated to the ethyl ester of 2-cyanonorbornane-2-carboxylic acid. The ester was converted to the dicyano derivative via the amide. 2-*exo*-cyanonorbornane (m.p. 25° C) and 2-*endo*-cyanonorbornane (m.p. 57° C) were prepared from the corresponding norbornenes by low pressure hydrogenation using Adam's catalyst.

Malono- and adiponitrile were commercially available materials, purified by fractional distillation immediately prior to use. Glutaronitrile (*8*), dimethylmalononitrile (*3*), diethylmalononitrile (*10*), tetramethylsuccinonitrile (*15*), tetraethylsuccinonitrile (*7*), 3,3-dimethylglutaronitrile (*20*), and 4,4-dimethylpimelonitrile (*14*) were prepared by previ-

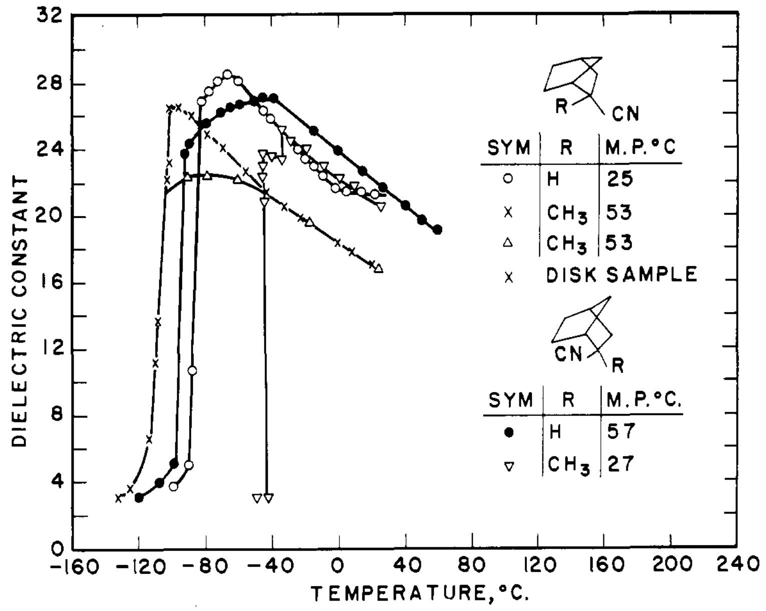


Figure 3. Dielectric constant as a function of temperature for a series of *endo*- and exo-cyanonorbornanes

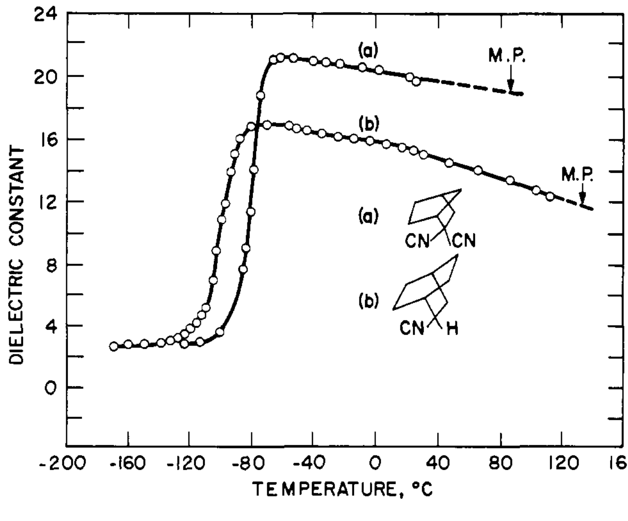


Figure 4. Dielectric constant as a function of temperature for 2-cyanobicyclooctane and 2,2-dicyanonorbornane

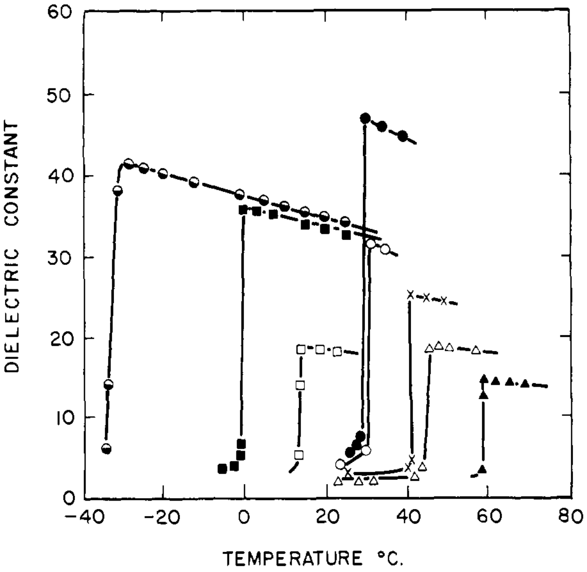
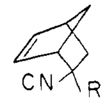


Figure 5. Dielectric constant as a function of temperature for several aliphatic dinitriles exhibiting "normal behavior"

Sym.	Compound	M.P., °C
●	Malononitrile	32.1
○	Dimethylmalononitrile	35.5–36.5
X	Diethylmalononitrile	44–46
△	Tetraethylsuccinonitrile	47–49.5
◒	Glutaronitrile	−29
■	Adiponitrile	0–1
□	Dimethylpimelonitrile	14–15
▲	Diethylpimelonitrile	59–60

Table I. Physical Properties of 2-*exo*-alkyl-2-*endo*-cyanonorbornenes



Where R Equals	Boiling Pt., °C/ Mm of Hg	Melting Pt., °C	Index of Refraction at 25° C	Density at 25° C, G/Cc
H	81/14	23-24	1.4866	1.0074
CH_3	103/30	46-47	. . .	. . .
C_2H_5	92/7	−7	1.4820	0.97526
C_3H_7	90/4	−15–−16	1.4789	0.95803
nC_4H_9	100/3	5	1.4778	0.94673
iC_4H_9	94/3.5	15	1.4794	0.94944
nC_5H_{11}	110/2.5	−2	1.4770	0.93745

ously described procedures. 3,3-Diethylglutaronitrile (m.p. 29–30° C) was prepared by the procedure of Sugiharra *et al.* (*20*) and 4,4-diethylpimelonitrile (m.p. 59–60° C) was prepared using a sequence similar to the one used by Miller and Adams (*14*).

MEASUREMENTS

Dielectric Constant and Dipole Moment. A coaxial two-terminal cell having a capacitance of about 25 pF was calibrated with spectrograde cyclohexane and used to measure the dielectric constant of the bulk materials as a function of temperature. The temperature was monitored

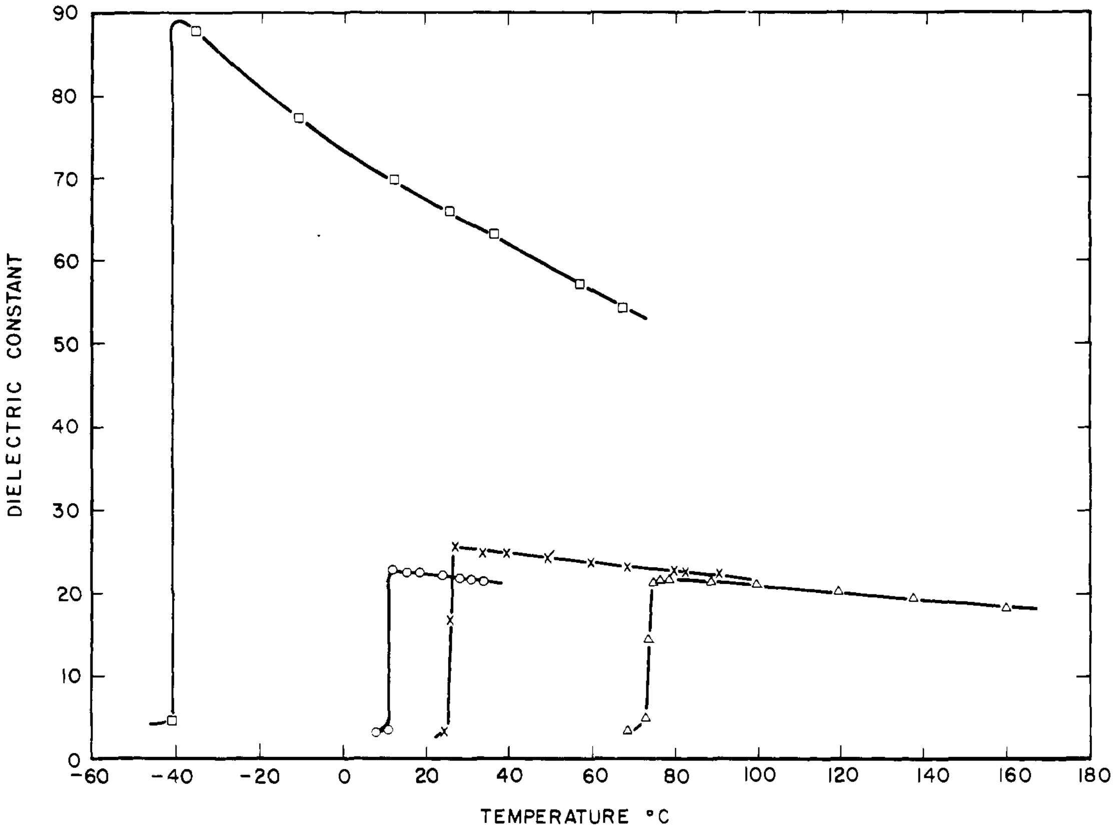


Figure 6. Dielectric constant as a function of temperature for several aliphatic dinitriles exhibiting solid-rotator behavior

Sym.	Compound	M.P., °C
X	Dimethylglutaronitrile	101–02
○	Diethylglutaronitrile	29–30
△	Tetramethylsuccinonitrile	167
□	Succinonitrile (from ref. *21*)	54.2

with a Chromel-Alumel thermocouple mounted in the wall of the test cell. The thermocouple was calibrated against a NBS certified thermometer. Dielectric constants were determined by comparing the cell capacitance with a NBS secondary standard at 10^5 Hz using a General Radio Co. Schering-type capacitance bridge. The cell had a plug that could be screwed downward, exerting sufficient pressure to prevent separation of the material from the electrodes at low temperatures. Dielectric measurements of the *endo*-methyl derivatives of cyanonorbornene and norbornane were also made in a conventional spring-loaded cell used for solid disk specimens. The dielectric constant *vs.* temperature behavior of the bicyclic and aliphatic compounds is illustrated in Figures 1 to 6; corresponding dipole freeze-out temperatures are recorded in Table II.

For the dipole moment measurements, dielectric constant and specific volume were determined for several dilute solutions of each material. Concentrations ranged from 0.001 to 0.012 in mole fraction of solute; spectrograde cyclohexane and benzene were used as solvents for the bicyclic and aliphatic compounds, respectively. A three-terminal dielectric cell as described in ASTM Method D 150-59T (*2*) was employed, measurements being made at 10^3 Hz and 25° C. Solution densities were determined using a 25-ml capacity pycnometer which had been calibrated against distilled water at 25° C. The above parameters were plotted as a function of mole fraction of solute, resulting in straight lines, intercept and slope being obtained by the method of least squares. The molar refractions were calculated from measured densities and refractive indices for liquids and from standard values of atomic refractivities (*12*) for the solids. The atomic polarization was estimated at 5% of the electronic polarization, the composite distortion polarization taken as 1.05 MR_D. The dipole moment was determined by the method of Halverstadt and Kumler (*9*). Table III presents the summarized data, with the computations performed on an IBM 7094 computer.

Table II. Melting Point, Dipolar Freeze-Out, and Rotational Range for a Variety of Bicyclic Nitriles and Aliphatic Dinitriles

Compound	Melting Point, °C	Dipolar Freeze-Out, °C	Rotational Range, °C
Norbornene			
Exo-cyano-*endo*-			
Hydrogen	8	−10	18
Methyl	64	−48	112
Ethyl	11	11	0
Endo-cyano-*exo*-			
Hydrogen	24	−43	67
Methyl	46	−5	51
Ethyl	−7	−7	0
Propyl	−16	−16	0
n-Butyl	5	5	0
Isobutyl	15	15	0
Pentyl	−2	−2	0
Norbornane			
Exo-cyano-*endo*-			
Hydrogen	25	−87	112
Methyl	53	−102	155
Ethyl	[a]	...	...
Endo-cyano-*exo*-			
Hydrogen	57	−98	155
Methyl	27	−45	72
2,2-Dicyano	95	−80	175
2-Cyanobicyclooctane	130	−100	230
Dimethylmalononitrile	35.5–36.5	36.5	0
Diethylmalononitrile	44–46	46	0
Tetramethylsuccinonitrile	167	75	92
Tetraethylsuccinonitrile	47–49.5	49.5	0
3,3-Dimethylglutaronitrile	101–102	25	77
3,3-Diethylglutaronitrile	29–30	11	19
4,4-Dimethylpimelonitrile	14–15	15	0
4,4-Diethylpimelonitrile	59–60	60	0

[a] Supercooled.

RESULTS AND DISCUSSION

The dielectric constant *vs.* temperature behavior of the bicyclic materials shown in Figures 1, 2, 3, and 4 appears to fit the preconceived idea that the spherical molecules exhibit rotator behavior whereas compounds that have alkyl side chains larger than methyl do not. In most cases a high melting point is paired with a wide range of rotation. The only exception is *endo*-cyanonorbornene, which has a lower melting point than *endo*-cyano-*exo*-methylnorbornene but a wider range of rotation.

Inspection of the dielectric curves reveals that for the rotators, even though we find high dielectric constants in the solid state, the classical pattern is not observed. Normally the dielectric constant increases because of density changes until the transition temperature is reached, and then ϵ_0 declines sharply to a small value that approximates the square of the index of refraction. In most of the bicyclic rotators studied we do not observe this sudden decrease in dielectric constant but rather a gradual decrease in ϵ_0 after it has reached a maximum. The usual rotator behavior is observed only in compounds that have their nitrile group in the *endo* position. It would appear therefore that normal rotator behavior is associated with the position in which the cyano group finds itself in the molecule. The cyano group, when in the *endo* position, is shielded by the hydrocarbon moiety of the molecule and cannot interact with other CN groups of neighboring molecules. The opposite is true where the nitrile group is in the *exo* position and therefore readily available for intermolecular interactions. On the other hand, if we turn to the aliphatic dinitriles, we observe that the materials shown in Figure 5 display normal behavior at their melting point. Only three of the materials studied are rotators—3,3-dimethylglutaro-, 3,3-diethylglutaro-, and tetramethylsuccinonitrile—and are shown in Figure 6, which also includes the dielectric constant *vs.* temperature curve of the closely related succinonitrile taken from White and Morgan (*21*). The fact that all the remaining aliphatic dinitriles fail to show rotational behavior is interesting, since molecular models indicate that they are spherical. The latter property is also evidenced by the high melting points of dimethylmalono-, diethylmalono-, and diethylpimelonitrile, and also by the fact that these materials exhibit plasticity in the solid phase, a property usually associated with rigid rotators. However, this same behavior has been observed by Clemett and Davies (*5*) for pivalonitrile, a molecule which *a priori* would be expected to have a solid rotator phase but does not, even though its melting point is abnormally high.

In an attempt to correlate the observed dielectric properties with structure, the dipole moments of the materials under investigation were determined from dilute solutions in benzene or cyclohexane. The observed dipole moments listed in Table III are in the expected range, based on both the geometrical configuration of the nitrile groups and values previously reported in the literature for aliphatic- and alicyclic mono- and dinitriles. With reference to the *exo*- and *endo*-cyanonorbornenes, the former has a smaller dipole moment, which is to be expected, since the inherent dipole contribution of the hydrocarbon (bicyclic) part of the molecule is partially opposed to that of the cyano group (*11*). Therefore, reinforcement of the two moments in the *endo*-cyanonorbornenes gives a higher resultant dipole moment. This trend is seen in both the methyl and ethyl members of the series. The dipole moments of the nonrotator *exo*-alkyl-*endo*-cyanonorbornenes lie in the range of 3.78 to 3.92D. The low value for isobutyl (3.78D) may be a reflection of a maximum accumulation (dense packing) of methyl groups. There is no significant difference between the observed dipole moments of the *endo*- and *exo*-cyanonorbornanes. It may therefore be concluded that in norbornenes the angle between the dipole of the bicyclic structure and that of the cyano group is dependent on the latter's position (*endo-exo*), whereas in the norbornanes there is no such dependence. As to the aliphatic dinitriles, the dipole moment increases as the length of the substituted R group increases for the derivatives of malono-, glutaro-, and pimelonitrile (Table III). Substitution with a bulky group initiates intramolecular orientation, which results in a decreased azimuthal angle between adjacent nitrile groups and therefore an increased resultant vector dipole moment. A decrease in steric hindrance with the same over-all net effect results when one increases the number of methylene groups ($-CH_2-$) in the hydrocarbon backbone chain of the molecule. In the case of the tetramethyl and tetraethyl derivatives of succinonitrile, there is a decrease in the dipole moment relative to the parent compound (succinonitrile). It is apparent that the bulky methyl and ethyl groups restrict the freedom of intramolecular rotation necessary for orientation; consequently, the lower potential energy form of trans configuration appears to predominate.

The experimentally determined dipole moments were then compared with the dipole moments calculated using the Onsager equation (*18*). The Onsager dipole moment, obtained from the experimentally determined dielectric constant of the bulk material, will be of the same value as the measured dipole moment if no intermolecular association takes place for the spherical-type compounds under discussion. If the Onsager moment is larger than the experimental dipole moment ($\Delta\mu < 0$), it may be assumed that association is taking place, with the $C{\equiv}N$ dipoles lined up in parallel fashion, leading to an apparent higher dielectric constant than would be obtained if there was no intermolecular association. On the other hand, if the Onsager-dipole moment is smaller than that observed ($\Delta\mu > 0$), it may be assumed that association takes place; in this case, however, the $C{\equiv}N$ dipoles are lining up in antiparallel fashion. In the ideal case the Onsager and observed dipole moments are identical ($\Delta\mu = 0$) and the material behaves like a normal liquid or solid rotator, with no intermolecular interaction. The differences in dipole moment ($\Delta\mu$) between the calculated and observed values for these compounds are listed in Table IV. For the bicyclic compounds the agreement between the two moments is from fair to excellent

Table III. Determination of Dipole Moment for a Variety of Bicyclic Nitriles and Aliphatic Dinitriles by Method of Halverstadt and Kumler (9)

		From [Dielectric Constant of Soln., ϵ_{12}] *vs.* [Mole Fraction of Solute, N_2] Curves		From [Specific Vol. of Soln., V_{12}] *vs.* [Mole Fraction of Solute, N_2] Curves			
Solute	M_2, Molecular Wt. of Solute	ϵ_1, extrapolated dielectric constant of solvent	$\alpha' = (d\epsilon_{12}/dN_2)$	V_1, extrapolated specific vol. of solvent	$\beta' = (dV_{12}/dN_2)$	P_{20},[a] Solute Molar Polarization at Infinite Dilution	μ,[b] Dipole Moment
Norbornene							
Exo-cyano-*endo*-							
Hydrogen	119.168	2.0185	13.261	1.2924	−0.37898	298.92	3.59
Methyl	133.195	2.0157	13.881	1.2924	−0.40339	315.84	3.67
Ethyl	147.222	2.0135	14.470	1.2935	−0.43711	332.18	3.75
Endo-cyano-*exo*-							
Hydrogen	119.168	2.0158	14.721	1.2924	−0.39876	328.33	3.78
Methyl	133.195	2.0144	15.331	1.2921	−0.37203	345.93	3.86
Ethyl	147.222	2.0132	15.764	1.2922	−0.40103	358.84	3.92
Propyl	161.249	2.0138	15.360	1.2922	−0.40692	355.04	3.86
n-Butyl	175.276	2.0131	15.424	1.2924	−0.45746	359.98	3.86
Isobutyl	175.276	2.0166	14.835	1.2925	−0.46975	347.42	3.78
Pentyl	189.303	2.0133	15.499	1.2923	−0.46710	365.81	3.87
Norbornane							
Exo-cyano-*endo*-							
Hydrogen	121.184	2.0134	15.324	1.2934	−0.37366	342.31	3.87
Methyl	135.211	2.0142	14.910	1.2936	−0.40171	337.86	3.81
Ethyl	149.238	2.0144	15.581	1.2923	−0.37298	356.24	3.90
Endo-cyano-*exo*-							
Hydrogen	121.184	2.0142	15.610	1.2927	−0.40770	347.08	3.90
Methyl	135.211	2.0187	15.343	1.2934	−0.37924	346.48	3.87
2,2-Dicyano	146.195	2.0169	22.025	1.2925	−0.55723	481.43	4.64
2-Cyanobicyclooctane	135.211	2.0163	15.302	1.2927	−0.46289	344.00	3.85
Dimethylmalononitrile	94.119	2.2774	21.635	1.1452	−0.03019	348.82	3.97
Diethylmalononitrile	122.173	2.2745	23.995	1.1452	−0.02981	393.47	4.18
Tetramethylsuccinonitrile	136.200	2.2736	12.330	1.1452	−0.09664	225.42	3.01
Tetraethylsuccinonitrile	192.308	2.2740	11.834	1.1452	−0.19299	235.02	2.93
3,3-Dimethylglutaronitrile	122.173	2.2751	22.936	1.1453	−0.14118	375.26	4.08
3,3-Diethylglutaronitrile	150.227	2.2756	27.272	1.1451	−0.19952	417.66	4.27
4,4-Dimethylpimelonitrile	150.227	2.2758	25.233	1.1459	−0.20296	417.26	4.26
4,4-Diethylpimelonitrile	178.281	2.2772	27.316	1.1459	−0.24059	456.34	4.43

[a] $P_{20} = [3\alpha' V_1/(\epsilon_1 + 2)^2]\, M_1 + (M_2 V_1 + M_1\beta')\, [(\epsilon_1 - 1)/(\epsilon_1 + 2)]$ where molecular weight of solvent $M_1 = 84.162$ (bicyclic nitriles) and $M_1 = 78.114$ (aliphatic dinitriles). [b] $\mu = 0.01281\, \{[P_{20} - (P_A + P_E)]T\}^{1/2}$ where $T = 298.1°$ K.

Table IV. Comparison of Dipole Moments of Bicyclic Nitriles and Aliphatic Dinitriles Observed in Dilute Solution and Obtained by Onsager Equation

	Dipole Moment, Debye Units		
Compound	Dilute soln.	Onsager[a]	$\Delta\mu$
Norbornene			
Exo-cyano-*endo*-			
Hydrogen	3.59	3.11	0.48
Methyl	3.67	3.16	0.51
Ethyl	3.75	3.54	0.21
Endo-cyano-*exo*-			
Hydrogen	3.78	3.62	0.16
Methyl	3.86	3.64	0.22
Ethyl	3.92	3.97	−0.05
Propyl	3.86	3.88	−0.02
n-Butyl	3.86	3.99	−0.13
Isobutyl	3.78	3.96	−0.18
Pentyl	3.87	3.98	−0.11
Norbornane			
Exo-cyano-*endo*-			
Hydrogen	3.87	3.50	0.37
Methyl	3.81	3.35	0.46
Ethyl	3.90	. . .	. . .
Endo-cyano-*exo*-			
Hydrogen	3.90	3.72	0.18
Methyl	3.87	3.76	0.11
2,2-Dicyano	4.64	4.02	0.62
2-Cyanobicyclooctane	3.85	3.25	0.60
Malononitrile	3.59[b]	4.20	−0.61
Dimethyl	3.97	4.11	−0.14
Diethyl	4.18	4.21	−0.03
Succinonitrile	3.93[b]	5.45	−1.52
Tetramethyl	3.01	4.21	−1.20
Tetraethyl	2.93	4.38	−1.45
Glutaronitrile	3.91[b]	4.37	−0.46
3,3-Dimethyl	4.08	4.12	−0.04
3,3-Diethyl	4.27	4.07	0.20
Pimelonitrile	4.10[b]	. . .	. . .
4,4-Dimethyl	4.26	3.74	0.52
4,4-Diethyl	4.43	3.86	0.57

[a] $\mu^2 = \frac{9kT}{4\pi N}\frac{M}{D}\frac{(2\epsilon_0 + \epsilon_\infty)(\epsilon_0 + 2)}{3\epsilon_0(\epsilon_\infty + 2)}\left(\frac{\epsilon_0 - 1}{\epsilon_0 + 2} - \frac{\epsilon_\infty - 1}{\epsilon_\infty + 2}\right)$

[b] From (*13*).

for the *endo*-cyanonorbornenes and norbornanes. This is not surprising, since the location of the nitrile group in the *endo* position makes it unavailable for intermolecular association. In the remaining norbornanes and in cyanobicyclo[2,2,2]octane $\Delta\mu > 0$, indicating that these materials are associated, with the $C{\equiv}N$ dipoles lined up in antiparallel fashion. This may also explain why in the bicyclic rotators where $\Delta\mu > 0$ we do not find a sharp drop at the transition point but rather a slow decrease of dielectric constant, indicating an increase of the amount of association as temperature decreases.

In the case of the aliphatic dinitriles we find $\Delta\mu$ varying from −1.52 to +0.57. 3,3-Dimethyl- and 3,3-diethylglutaronitrile have $\Delta\mu$ close to zero and show rotational freedom in the solid state. We must conclude that in these compounds the neopentyl-type system affords a shield around the nitrile groups, making intermolecular association difficult, as was the case with the *endo*-cyanides in the bicyclic compounds. The other rotators in this group, succinonitrile and tetramethylsuccinonitrile, display very large negative $\Delta\mu$ values, indicating parallel alignment of the molecules. Williams and Smyth (*22*) have pointed out that in the case of succinonitrile rotation probably does not occur with the molecule in a spherical envelope but rather in a cylindrical one, which would allow cooperative rotation of head-to-head aligned clusters of molecules; our measurements do not allow us to distinguish between these two types of rotation. The steep slope of dielectric constant *vs.* temperature in succinonitrile may also be explained by increased association and hence rapid increase of apparent dipole moment of the bulk material. The same arguments might explain the behavior of tetramethylsuccinonitrile, except that the slope of its dielectric constant *vs.* temperature appears to be normal.

In the malononitriles $\Delta\mu$ approaches zero as the size of the substituent is increased, indicating again that the CN groups become less available to association as steric crowding takes place around them. In the pimelonitriles no change can be observed; presumably, the alkyl groups are too far removed from the nitrile groups to influence their surroundings. However, the latter compounds are the only ones in this group displaying a positive $\Delta\mu$, indicating antiparallel association, thus behaving like the *exo*-bicyclic nitriles and the mononitriles discussed by Dannhauser and Flueckinger (*6*).

Depending upon the environment in which the cyano group finds itself, nitriles may be associated in either parallel or antiparallel fashion, or in very special cases not at all. Where the cyano group is not crowded by bulky hydrocarbon residues as in the *exo*-norbornenes, *exo*-norbornanes, and pimelonitriles, the preferred configuration is the antiparallel association. Otherwise a parallel arrangement is preferred, except for special cases (*endo*-cyano bicyclics and disubstituted glutaronitriles) where no intermolecular association is possible.

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