Rotational Isomerism in 1,1′-Dicyanobicyclopentyl, 1,1′-Dicyanobicyclohexyl, and 1,1′-Dicyanobicycloheptyl

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I.r. spectra of 1,1′-dicyanobicyclopentyl, 1,1′-dicyanobicyclohexyl, and 1,1′-dicyanobicycloheptyl in the solid and solution states, and Raman spectra in the solid state are reported and assignment of frequencies made. Dipole moments in different solvents (benzene, carbon tetrachloride, and dioxane) at different temperatures and molar Kerr constants (in carbon tetrachloride and benzene) are also reported. Analysis of the dielectric data shows that, at 25 °C, the compounds in the series exist as rotameric mixtures in carbon tetrachloride solution containing 4.5, 11, and 38% respectively of the *gauche* rotamer. Benzene causes the *gauche* population to increase, as evidenced by the dipole moment and Kerr constant values in this solvent. Comparison of the Raman and i.r. spectra of the solids suggests that all three compounds exist in the *trans* conformation in the solid state.

Studies of rotational isomerism in 1,2-dicyanoethane[1,2] and 2,3-dicyano-2,3-dimethylbutane[3,4] have revealed contrasting physical properties in the two compounds. Steric and polar factors have been invoked to account for the difference in their dihedral angles (93 and 85°, respectively) and in their *gauche* content: 75 (in benzene) and 18% (in carbon tetrachloride), respectively. To examine further the influence of these factors, we have prepared and studied the compounds 1,1′-dicyanobicyclopentyl, 1,1′-dicyanobicyclohexyl, and 1,1′-dicyanobicycloheptyl. These compounds may be regarded as symmetrically substituted ethanes, the three hydrogen atoms on each of the two ethane carbon atoms being replaced by a cyano group and the two carbon members of the ring system. Rotational isomerism involving the *trans* and *gauche* conformations can be expected.

Experimental

Solutes.—1,1′-Dicyanobicyclohexyl was prepared by refluxing 1,1′-azobis(cyclohexane-1-carbonitrile) with toluene while 1,1′-dicyanobicyclopentyl and 1,1′-dicyanobicycloheptyl were prepared by the method described by Overberger and Berengaum[5] involving hydrazine sulphate, sodium cyanide, and cyclopentanone and cycloheptanone, respectively.

Solvents.—All solvents were carefully distilled and/or fractionated and dried before use. The physical constants associated with their use in dielectric and Kerr effect measurements have been previously given.[4,6]

Apparatus.—Dielectric constants were determined with a heterodyne-beat meter[7] and densities and refractive indices by standard procedures.[8] Kerr constants were measured photometrically.[9]

Solid-state i.r. spectra were recorded as Nujol and hexachlorobutadiene mulls and as KBr pressed-disc samples. Solution-state spectra were obtained using solvents like carbon tetrachloride, carbon disulphide, benzene, chloroform, and acetonitrile. The Perkin-Elmer 682 spectrophotometer was used for all these i.r. measurements. Raman measurements were made using the 514.5 nm line of a coherent CR-6 argon-ion laser. The spectra were recorded with a Spex 1403 double monochromater in conjunction with a photon-counting system set up in the Physics Department, National University of Singapore.

Results and Discussion

The results of all these physical measurements are presented in Tables 1 and 2 with standard notation.

Conformers of 1,1′-*Dicyanobicyclopentyl.*—Figure 1 shows a diagram of the C_{2h} *trans* conformation of 1,1′-dicyanobicyclopentyl. Various conformations of the cyclopentane ring have been proposed.[10–17] These are shown in Figure 2. For conformations (a) and (b), the number of carbon atoms that lie in one plane are four and three, respectively. Conformation (a) is often called the 'envelope form' with C_s symmetry. Conformation (c) is a structure proposed by Le Fèvre[10] to account for the data from molar Kerr constant data. In this configuration, the mutual repulsions of C–H bonds are uniform. The disposition of the carbon atoms of the ring can be described as follows: If X, M, and Y are the mid-points of DE, CD, and BC, respectively, then A, X, M, and Y lie on one plane.

The projections of B–E on this plane are at B′–E′, where BB′ = CC′ = DD′ = EE′ = 0.32 Å. The angles at A, C, and D are in the order 111, 108, and 108° and the C–C distance 1.54 Å. Then AB and AE lie at an angle R to the horizontal (AMXY plane), where R = 12° 1′, and CD, BC, and DE lie at angle S to the horizontal, where S = 24° 36′. Angle P is the projection of BCD on B′CD′ in the horizontal plane minus 90°, P = 35° 40′;

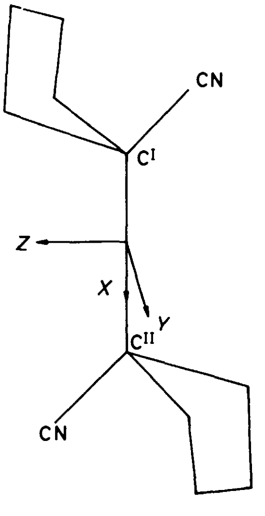


Figure 1. *trans* Conformer of 1,1′-dicyanobicyclopentyl

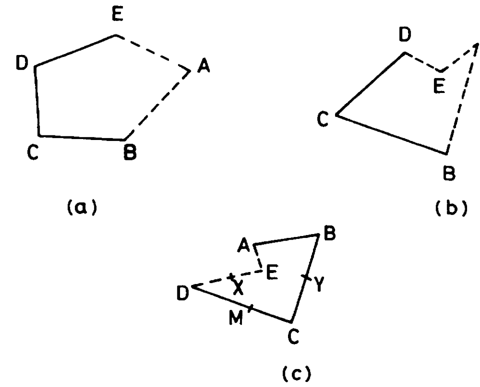


Figure 2. Possible conformations of the cyclopentane ring

Q = B′AE′/2 = 54° 38′ where B′AE′ is the projection of BAE in the horizontal plane. This is the model used for our calculations of the theoretical Kerr constants for 1,1′-dicyanobicyclopentyl. In the light of all the above, we have implicitly assumed that a σ_h plane exists in *trans*-1,1′-dicyanobicyclopentyl which bisects the cyclopentane rings. This would also occur if the rings were of the envelope form with C_s symmetry.

The *gauche* conformer possesses only a C_2 axis of symmetry which bisects the dihedral angle formed by the two C–CN bonds.

Dipole moment and Kerr constant measurements. Data from dipole measurement of 1,1′-dicyanobicyclopentyl in CCl_4 at 7, 25, and 45 °C, in C_6H_6 at 25, 45, and 60 °C, and in dioxane at 25 °C are summarized in Table 2(a). Kerr effect measurements in C_6H_6 and CCl_4 at 25 °C are also listed there.

The non-planar model for the cyclopentyl rings proposed by Le Fèvre[10] was adopted for these calculations. Bond or group

Table 1. (a) I.r. and Raman spectra of 1,1′-dicyanobicyclopentyl

Nujol	HB	KBr	CCl_4 (7%)	C_6H_6 (8%)	$CHCl_3$ (10%)	CH_3CN (10%)	Raman solid	Approximate group assignment
2 980 (47)	2 980 (47)	2 983 (48)	2 980 (83)	2 980 (70)	2 980 (80)	2 980 (95)	2 981 (s)	ν C–H (as)
×	2 968 (47)	2 968 (48)	2 968 (82)	×	×	×	–	
×	–	–	–	×	×	×	2 939 (s)	
×	2 923 (47)	2 923 (41)	2 925 (10)	×	2 920 (17)	×	–	
×	2 880 (39)	2 880 (40)	2 885 (75)	2 880 (70)	2 885 (50)	×	2 871 (m)	ν C–H (sym)
2 240 (43)	2 240 (40)	2 240 (40)	2 240 (50)	2 240 (42)	2 240 (30)	2 240 (40)	2 238 (s)	ν C≡N
–	–	–	–	–	–	–	2 171 (w)	2 × ν CC
–	–	–	–	–	–	–	2 108 (w)	
×	1 450 (50)	1 450 (60)	1 457 (70)	1 453 (60)	1 457 (47)	×	1 449 (s)	δ CH_2 (ring)
1 330 (24)	1 330 (35)	1 330 (38)	1 328 (38)	1 325 (30)	1 325 (20)	1 328 (19)	1 329 (m)	δ CCH
1 310 (10)	1 310 (17)	1 310 (20)	–	–	–	–	–	
1 285 (0.5)	–	1 285 (3)	–	–	–	–	1 287 (m)	
1 262 (2)	1 262 (6)	1 262 (11)	1 265 (5)	1 268 (4)	–	–	–	
1 227 (2)	1 228 (2)	1 227 (8)	1 228 (7)	–	–	–	–	
1 203 (7)	1 203 (2)	1 203 (31)	1 203 (16)	1 200 (22)	×	1 200 (15)	1 209 (m)	ν C–C
–	×	–	–	×	×	–	1 187 (m)	
1 080 (sh)	×	1 080 (1)	1 080 (sh)	×	–	–	–	
–	–	1 052 (4)	–	×	–	×	–	
–	–	1 040 (25)	–	×	–	×	–	
1 032 (22)	1 032 (25)	1 032 (25)	1 032 (12)	×	1 030 (4)	×	1 033 (s)	
980 (29)	980 (44)	980 (31)	980 (17)	980 (13)	980 (10)	980 (10)	–	ν C–CN (sym) ν C–CN (as)
955 (1)	×	955 (1)	–	–	–	–	–	
937 (25)	937 (33)	937 (33)	939 (25)	938 (19)	938 (10)	935 (15)	–	
920 (28)	920 (28)	920 (28)	920 (5)	920 (3)	920 (2)	×	921 (w)	
888 (10)	888 (8)	888 (18)	895 (5)	897 (4)	890 (3)	×	889 (s)	
800 (25)	×	800 (30)	×	×	×	×	–	
–	×	–	–	850 (4)	850 (2)	–	–	
–	–	752 (1)	×	×	×	×	–	ν C–C and δ ring
×	–	734 (1)	×	×	×	×	739 (w)	
–	–	–	×	–	×	–	723 (w)	
666 (sh)	×	670 (7)	–	×	×	680 (2)	–	
542 (10)	542 (15)	542 (13)	543 (6)	543 (6)	–	550 (5)	553 (m)	δ ring + δ CCN + δ CN–C–CN
–	–	–	–	–	–	–	520 (s)	
–	–	509 (2)	–	–	–	–	512 (m)	
472 (32)	472 (35)	473 (37)	475 (15)	480 (14)	475 (8)	482 (12)	–	
–	–	–	–	–	–	–	429 (s)	
–	–	–	–	–	–	–	419 (m)	
		400 (2)						
		387 (2)						
		378 (3)					371 (s)	
		370 (2)						
		348 (32)	340 (5)					
		330 (10)						
		320 (5)						
		304 (8)						
		290 (8)						
		280 (4)						

× Indicates masking by background solvent or mulling agent, – indicates absence of absorption, sh = shoulder, br = broad. The numbers or letters in parentheses indicate relative intensities.

Table 1 (*continued*)

(b) I.r. and Raman spectra of 1,1′-dicyanobicyclohexyl

Nujol	HB	KBr	C_6H_6 (5.6%) 2.284	$CHCl_3$ (2.3%) 4.806	CH_3CN (6.0%) 37.5	Raman solid	Approximate group assignment
×	–	3 223 (3)	×	×	×	–	ν C–H (as)
×	–	3 170 (3)	×	×	×	–	
×	2 983 (40)	2 983 (67)	×	2 980 (2)	×	2 983 (s)	
×	2 970 (48)	2 970 (70)	×	×	×	2 972 (m)	
×	2 950 (63)	2 950 (75)	×	×	×	2 949 (s)	
×	2 938 (63)	2 938 (74)	×	×	×	–	
×	–	–	×	×	×	2 905 (m)	
×	2 870 (58)	2 872 (74)	2 878 (58)	2 865 (51)	2 875 (25)	2 871 (s)	ν C–H (sym)
×	–	2 810 (33)	×	×	×	–	
×	–	2 698 (19)	–	–	–	–	2 × δ CCH
2 680 (3 sh)	–	2 678 (19)	–	–	–	–	ν C≡N
2 240 (31)	2 240 (30)	2 240 (54)	2 240 (6)	2 240 (16)	×	2 238 (s)	
–	–	–	–	–	–	2 172 (m)	2 × ν CC
–	–	–	–	–	–	2 108 (m)	
–	–	–	1 530 (5)	–	1 540 (5)	–	δ CH_2 (ring)
×	1 471 (16)	1 471 (42)	–	–	×	–	
×	1 453 (60)	1 453 (76)	1 458 (36)	1 460 (65)	×	–	
×	1 440 (26)	1 440 (60)	–	–	×	1 447 (s)	
×	–	1 400 (2)	1 400 (4)	–	×	–	δ CCH
×	1 365 (23)	1 362 (43)	1 360 (7)	1 360 (17)	1 375 (25)	1 359 (s)	
1 357 (24)	–	1 357 (55)	–	–	×	–	
1 340 (8)	1 340 (10)	1 340 (37)	×	1 345 (6)	×	–	
1 330 (3)	1 330 (5)	1 330 (23)	×	–	×	–	
–	–	–	–	–	×	1 305 (w)	
1 295 (10)	1 297 (17)	1 295 (47)	×	–	×	–	
1 285 (8)	1 285 (12)	1 285 (36)	1 290 (4)	1 290 (10)	1 290 (3)	1 287 (w)	
1 260 (3)	1 260 (4)	1 260 (16)	1 265 (5)	1 265 (10)	1 260 (4)	1 273 (s)	
–	–	–	–	×	–	1 223 (s)	ν C–C
–	×	–	×	×	×	1 193 (m)	
1 179 (4)	1 179 (21)	1 179 (18)	1 180 (2)	–	–	–	
1 150 (30)	1 150 (44)	1 150 (70)	1 150 (8)	1 150 (20)	1 150 (13)	1 149 (w)	
–	–	–	–	–	–	1 097 (m)	
–	–	1 084 (7)	1 084 (3)	–	–	–	
–	–	–	–	–	×	1 079 (m)	
–	×	–	×	–	×	1 052 (s)	
1 035 (20)	1 038 (18)	1 032 (47)	1 035 (10)	–	1 032 (12)	–	
1 011 (35)	1 011 (25)	1 011 (63)	1 012 (8)	1 013 (16)	×	–	
–	×	–	×	950 (4)	950 (2)	953 (m)	ν C–CN (sym)
933 (48)	933 (47)	933 (73)	935 (12)	933 (18)	933 (8)	–	
–	–	–	–	–	×	915 (m)	ν C–CN (as)
902 (20)	903 (15)	902 (48)	903 (3)	903 (6)	903 (3)	–	
868 (30)	868 (42)	866 (59)	866 (10)	867 (18)	863 (6)	–	
–	×	–	850 (2)	×	850 (2)	859 (s)	
–	×	–	–	×	×	843 (m)	
820 (3)	–	820 (14)	–	×	×	–	
798 (19)	798 (51)	797 (60)	–	×	×	–	ν C–C and δ (ring)
740 (4)	–	740 (5)	×	×	×	–	
–	–	–	×	×	×	668 (s)	
639 (2)	–	639 (8)	×	630 (3)	–	–	
–	–	577 (3)	×	–	–	–	
438 (11)	438 (15)	438 (31)	×	440 (2)	×	–	δ (ring) + δ CCN + δ CN–C–CN
409 (19)	409 (18)	409 (37)	×	409 (6)	×	–	
402 (18)	405 (18)	402 (46)	×	405 (7)	×	–	
390 (7)	390 (23)	390 (39)	×	×	×	–	
×	–	342 (5)	×	×	×	–	

(c) I.r. and Raman spectra of 1,1′-dicyanobicycloheptyl

Nujol	HB	KBr	CCl_4 (3%)	C_6H_6 (3%)	$CHCl_3$ (7%)	CH_3CN (9%)	Raman solid	Approximate group assignment
×	–	–	–	×	×	×	2 980 (m)	ν C–H (as)
×	2 950 (68)	2 950 (80)	2 945 (67)	2 945 (87)	2 945 (85)	2 945 (70)	2 943 (s)	
×	–	–	–	×	×	×	2 936 (s)	
×	–	–	–	×	–	×	2 917 (s)	
×	–	–	–	×	–	×	2 903 (m)	

Table 1 (*continued*)

(c) I.r. and Raman spectra of 1,1′-dicyanobicycloheptyl (*continued*)

Nujol	HB	KBr	CCl_4 (3%)	C_6H_6 (3%)	$CHCl_3$ (7%)	CH_3CN (9%)	Raman solid	Approximate group assignment
×	2 880 (62)	2 880 (78)	2 875 (42)	2 875 (70)	2 875 (70)	2 875 (54)	2 875 (m)	ν C–H (sym)
2 710 (5)	2 710 (3)	2 710 (5)	2 710 (3)	2 710 (5)	2 710 (4)	×	–	2 × δ CCH
2 240 (30)	2 240 (32)	2 240 (50)	2 240 (8)	2 240 (22)	2 240 (30)	2 240 (15)	2 240 (s)	ν C≡N
×	1 465 (60)	1 465 (83)	1 465 (42)	1 465 (44)	1 465 (75)	×	1 455 (s)	δ CH_2 (ring)
×	1 450 (53)	1 450 (82)	1 450 (32)	1 450 (58)	1 450 (59)	×	1 448 (s)	
×	1 375 (6)	1 375 (20)	1 370 (6)	1 370 (13)	1 370 (12)	×	1 379 (w)	δ CCH
1 355 (14)	1 355 (8)	1 355 (22)	–	1 355 (13)	1 355 (12)	1 355 (5)	1 364 (w)	
1 305 (5)	1 301 (5)	1 301 (10)	1 300 (2)	1 300 (5)	1 300 (6)	1 300 (4)	1 289 (w)	
1 273 (2)	1 273 (4)	1 273 (3)	–	1 270 (6)	1 270 (4)	1 270 (2)	–	
–	–	–	×	1 240 (3)	×	1 235 (2)	–	
–	–	–	–	–	–	–	–	
1 223 (10)	1 223 (13)	1 220 (20)	1 213 (3)	–	×	–	–	ν C–C
1 205 (13)	1 205 (5)	1 205 (30)	–	1 210 (9)	×	1 210 (5)	–	
1 135 (11)	1 135 (4)	1 135 (22)	–	×	×	×	1 137 (s)	
1 130 (4)	–	1 130 (12)	–	×	–	–	–	
1 122 (4)	1 120 (4)	1 122 (10)	–	–	–	–	–	
–	–	–	–	–	–	–	–	
1 073 (18)	1 072 (19)	1 072 (36)	1 080 (4)	1 080 (9)	1 080 (10)	1 080 (6)	1 085 (m)	
–	×	1 058 (3)	–	–	–	–	1 065 (m)	
1 043 (16)	1 040 (19)	1 040 (26)	1 035 (2)	×	1 035 (5)	×	1 043 (s)	
–	×	–	–	990 (3)	–	–	–	
915 (5)	×	965 (15)	–	–	–	×	–	ν C–CN (sym)
955 (6)	×	955 (14)	–	955 (7)	955 (8)	955 (4)	–	
945 (21)	945 (56)	945 (41)	945 (5)	945 (10)	945 (10)	945 (14)	939 (w)	
–	×	900 (2)	–	–	–	–	900 (w)	ν C–CN (as)
867 (19)	×	867 (32)	–	×	×	–	–	
845 (13)	×	845 (25)	–	845 (10)	–	850 (5)	855 (m)	
816 (19)	×	816 (35)	×	815 (5)	×	815 (3)	–	ν C–C and δ ring
–	×	–	×	×	×	×	793 (s)	
×	×	–	×	770 (6)	×	770 (4)	–	
743 (15)	740 (16)	743 (30)	×	735 (4)	×	×	–	
–	×	–	×	675 (3)	×	×	–	
–	×	–	–	×	×	–	649 (s)	
569 (4)	569 (9)	569 (12)	–	–	–	–	–	
–	–	524 (2)	–	–	–	–	512 (m)	δ ring + δ CCN δ CN–C–CN
–	–	–	–	–	–	–	497 (w)	
480 (11)	480 (21)	480 (22)	–	×	×	×	–	
–	–	445 (2)	–	–	–	–	–	
–	–	440 (2)	–	–	–	–	–	
		395 (10)						
		390 (4)						
		380 (2)						
		375 (3)						
		373 (10)						
		347 (4)						

polarizability values utilized are listed in Table 3. Based on the variations of the *gauche* population ($x\%$) with the dihedral angle (2φ) from both Kerr constant and dipole moment data, plots of $x\%$ *versus* 2φ can be made[4] (Table 4). The intersection of the curves gives the equilibrium distribution of *gauche*-conformers for the particular solvent, corresponding to a particular value of 2φ obtained at the point of intersection. In this instance, values of $x\% = 4.5$ and $2\varphi = 82°$ are obtained for CCl_4 solution. Substituting these values into the Boltzmann equation $N_g/N_t = 2\exp(-\Delta E_s/RT)$ gives a value of 9.3 kJ mol^{-1} for ΔE_s.

The graphical method of Lennard-Jones and Pike[20] affords an alternative method of obtaining ΔE_s based on the temperature dependence of the dipole moment. Application of this method on our data also gives a value of 9.3 kJ mol^{-1} for ΔE_s in CCl_4 and a dihedral angle of 85°. For benzene solution, ΔE_s and 2φ were found to be 6.5 kJ mol^{-1} and 103°, respectively.

Table 5 gives the vibrational species associated with the *trans* and *gauche* conformers using standard spectroscopic notation.[21] Although the i.r. and Raman spectra of solid 1,1′-dicyanobicyclopentyl [Table 1(a)] show several coincident bands in the 3 000—700 cm^{-1} region, yet the rule of mutual exclusion holds for the 700—370 cm^{-1} region where bands are usually identifiable as being due to the skeletal modes of vibration involving the central carbon atoms of the ethane skeleton. This, combined with the fact that the *gauche* population in CCl_4 is so low (4.5%), strongly suggests that only the *trans*-rotamer is found in the solid state.

Very weak extra absorptions at 850 cm^{-1} in both $CHCl_3$ and C_6H_6 in the i.r. solution spectra indicate the minute presence of *gauche* conformers in agreement with our dielectric data. An interesting feature in the i.r. spectra of 1,1′-dicyanobicyclopentyl is the reversal of relative intensities of the bands at 921 and 888 cm^{-1} in going from the solid to solution states. The ratio of the intensities for the KBr spectrum is 1.56; for CCl_4 1.0; for C_6H_6

Table 2. Molar polarizations, refractions, dipole moments, and molar Kerr constants at infinite dilution of 1,1′-dicyanobicyclopentyl, 1,1′-dicyanobicyclohexyl, and 1,1′-dicyanobicycloheptyl. Incremental changes in the relative permittivities, densities, refractive indices, and Kerr constants ($\Delta\varepsilon$, Δd, Δn, and ΔB, respectively) were measured for solutions having solute weight fractions w_2. The coefficients α, β, γ, and δ were derived from the relations $\alpha\varepsilon_1 = \Sigma w e/\Sigma w_2$, $\beta d_1 = \Sigma\Delta d/\Sigma w_2$, $\gamma n_1 = \Sigma\Delta n/\Sigma w_2$, $\delta B_1 = \Sigma\Delta B/\Sigma w_2$. When the plots of $\Delta\varepsilon$ *versus* w_2 showed curvature, as in the case of benzene and dioxane solution, a regression formula of the type $\Delta\varepsilon = aw_2 + bw_2^2$ was used to fit each experimental curve and the coefficients *a* and *b* were determined. α was then derived from $\alpha\varepsilon_1 = a$. $_\infty(mK_2)$ refers to the solute molar Kerr constant at infinite dilution

Temperature (°C)	Solvent	Conc. range ($10^5\ w_2$)	$\alpha\varepsilon_1$	β	γ	δ	P_2/cm^3	R_D/cm^3	$10^{30}\mu$*/ C m	$10^{27}\ _\infty(mK_2)$/ m^5 V^{-2} mol^{-1}
(a) 1,1′-Dicyanobicyclopentyl										
7	CCl_4	509—976	1.09	−0.593			75.22	54.04	3.20 ± 0.10	
25	CCl_4	695—1 256	1.35	−0.576	0.038	12.4	81.01	54.00	3.60 ± 0.07	24
45	CCl_4	528—1 185	1.70	−0.488	0.155		86.75	54.26	4.04 ± 0.07	
25	Benzene	1 295—2 342	1.94	0.195	0.031	8.37	120.20	53.18	6.04 ± 0.03	130
45	Benzene	921—2 069	1.93	0.178			14.10	53.26	6.27 ± 0.03	
60	Benzene	538—1 249	1.83	0.165			123.40	53.18	6.44 ± 0.07	
25	Dioxane	452—1 254	2.24	0.173	0.200			52.96	5.57 ± 0.07	
(b) 1,1′-Dicyanobicyclohexyl										
7	CCl_4	173—289	3.15	−0.307			121.1		5.30 ± 0.13	
25	CCl_4	232—565	3.02	−0.454	0.077	2.25	126.7	62.8	5.74 ± 0.13	4.90
45	CCl_4	201—490	2.96	−0.462	0.156		128.8		6.17 ± 0.07	
25	Benzene	445—1 015	2.50	0.187	0.031	−16.79	161.4	63.05	7.20 ± 0.03	−307
45	Benzene	412—921	2.44	0.211			161.7		7.44 ± 0.07	
60	Benzene	579—105	2.42	0.220			163.5		7.71 ± 0.07	
25	Dioxane	355—113	2.68	0.057	0.149		152.3		6.77 ± 0.07	
(c) 1,1′-Dicyanobicycloheptyl										
7	CCl_4	464—1 463	*a*	−0.556			329.3		11.34 ± 0.03	
25	CCl_4	511—1 278	*b*	−0.501	0.158	−4.7	324.9	72.13	11.64 ± 0.03	−17
45	CCl_4	674—1 656	*c*	−0.436	0.188		315.7	71.62	11.81 ± 0.03	
25	Benzene	453—2 015	*d*	0.200	0.029	−17.2	445.2		14.18 ± 0.03	−422
25	Dioxane	868—1 764	9.25	0.058	0.155		436.7	71.92	13.91 ± 0.03	

* Calculated on the basis that $_DP = 1.05\ R_D$.

^{a} $10.38w + 78.95w_2^2$. ^{b} $9.97w + 76.58w^2$. ^{c} $9.31w + 64.91w^2$. ^{d} $8.25w + 19.55w^2$.

Table 3. Bond–group polarizabilities in 10^{23} cc†

Bond–group	*L*	*T*	*V*	Ref.
b_i (C–CN)	0.39	0.16	0.16	18
b_i (C–C)	0.098	0.026	0.026	10*a*
b_i (C–H)	0.065	0.065	0.065	10*a*
b_i'* (cyclopentyl)	0.832	0.761	0.684	19
b_i''* (cyclohexyl)	0.98	0.98	0.84	10*a*

* b_i' = Group polarizability of cyclopentyl (C_5H_9) based on the cyclopentane model adopted. b_i'' = Group polarizability of cyclohexyl (C_6H_{11}) based on the cyclohexane model adopted. † 1 cc = 1.113×10^{-16} C^2 m^2 J^{-1} (or C m^2 V^{-1}).

0.75; and for $CHCl_3$ 0.67. A possible reason for this reversal in relative intensities is that the conformations of the cyclopentyl ring in the solid and solution states are different.

An extra absorption at 1 040 cm^{-1} occurred in the i.r. spectrum of the KBr sample not observed in the case of Nujol and hexachlorobutadiene mulls or the solution spectra. The fact that this band was not observed in the solution-state spectra, especially in solvents of high dielectric constants like CH_3CN and $CHCl_3$, suggests that it is unlikely that this is an absorption due to a *gauche* conformer. It seems more likely that this band has arisen from ionic association with the matrix although the splitting of the i.r. bands of polyvinylidene fluoride at liquid

Table 4. Calculated dipole moments and molar Kerr constants with corresponding *gauche* percentage population for various conformations of 1,1′-dicyanobicyclopentyl and 1,1′-dicyanobicyclohexyl based on data in CCl_4

1,1′-Dicyanobicyclopentyl

Dihedral angle (°)	60	70	76	78	80	81	83	85	90
μ (calc.)	19.62	18.55	17.78	17.55	17.34	17.18	16.95	16.68	16.01
x%	3.37	3.77	3.91	4.20	4.31	4.38	4.52	4.66	5.08
m*K* (calc.)	653	569	471	440	410	395	366	338	273
x%	2.62	3.01	3.66	3.91	4.21	4.36	4.71	5.10	6.35

1,1′-Dicyanobicyclohexyl

Dihedral angle (°)	60	70	80	83	85	87	90
μ (calc.)	19.62	18.55	17.34	16.95	16.68	16.41	16.01
x%	8.56	9.57	10.90	11.46	11.80	12.20	12.80
m*K* (calc.)	201	116	42	25	10	−1.0	−17
x%	1.6	2.7	7.6	14.0	36.0		

Table 5. 1,1′-Dicyanobicyclopentyl: vibrational species

Vibrational species	Activity I.r.	Activity Raman	Total no. of fundamentals	Skeletal†	Non-skeletal
trans					
A_g $3n + 2n_h + n_2 - 1$	ia	p*	23	8	15
A_u $3n + n_h + n_2 + n_0 - 1$	a	v	20	5	15
B_g $3n + n_h + 2n_2 - 2$	ia	dp	19	4	15
B_u $3n + 2n_h + 2n_2 + 2n_o - 2$	a	v	22	7	15
gauche					
A $3n + n_o - 2$	a	p*	43	13	30
B $3n + 2n_o - 4$	a	dp *	41	11	30

† Refers to the atoms directly attached to the central carbons of the ethane skeleton.

nitrogen temperature has been attributed to the disorder in molecular packing of the crystals.[22]

The C–N stretching frequency is observed as an intense absorption at 2 240 cm^{-1} in the i.r. spectrum and at 2 238 cm^{-1} in the Raman spectrum of the solid state.

Conformers of 1,1′-*Dicyanobicyclohexyl.*—Figure 3 shows a diagram of the *trans* conformer of 1,1′-dicyanobicyclohexyl. The cyclohexyl rings are assumed to adopt the chair form rather than that of the boat in view of the findings of Hazebroek and Oosterhoff,[23] Barton,[24] Howlett,[25] Allinger,[26] and Hendrickson.[27] The relative dispositions of the rings may give rise to three possible configurations. They are such that the rings are attached by a bond which is: (a) equatorial to both rings (Figure 3); (b) axial to one ring but equatorial to the other (Figure 4); or (c) axial to both rings (Figure 5). Molecular models show that the structure where both bonds attaching the rings to the central carbon atoms are equatorial involves the least strain. Such a *trans* structure belongs to the C_{2h} point group, with the corresponding *gauche* conformer in the C_2 point group.

Dipole moment and Kerr constant measurements. Results of the dipole moment measurement of 1,1′-dicyanobicyclohexyl in CCl_4 at 7, 25, and 45 °C, in C_6H_6 at 25, 45, and 60 °C, and in dioxane at 25 °C are summarized in Table 2(b). Kerr effect measurements in CCl_4 and C_6H_6 are also recorded there.

We have calculated the percentage of *gauche* conformers corresponding to the various dihedral angles. The Kerr constants were calculated using the bond and group polarizabilities summarized in Table 3.

Plots of $x\%$ *versus* 2φ yielded $x\% = 11$ and $2\varphi = 82°$ for data in CCl_4 solution (Table 4). Substituting these values into the Boltzmann's equation gives a value of 6.9 kJ mol^{-1} for ΔE_s. The alternative method of Lennard-Jones and Pike[20] gives 6.6 kJ mol^{-1} for ΔE_s and a dihedral angle of 86°, in reasonable agreement with the preceding values. For measurements in C_6H_6 solution ΔE_s was 5.2 kJ mol^{-1} and the dihedral angle 84°. The dihedral angle of the *gauche* conformer in CCl_4 (82 or 86°) evaluated above may be compared with that of 85° for 2,3-dicyano-2,3-dimethylbutane and 93° for 1,2-dicyanoethane and there reflect the tendency for dihedral angles of the *gauche* conformer to be large in succinonitriles. This may be attributed to the strong dipolar repulsions between the highly polar cyano groups.

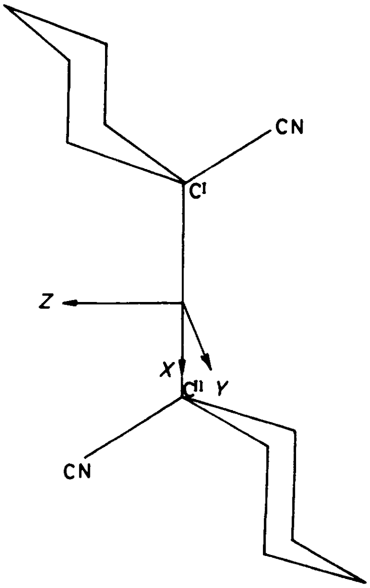


Figure 3. *trans* Conformers of 1,1′-dicyanobicyclohexyl where the central C–C bond is equatorial to both rings

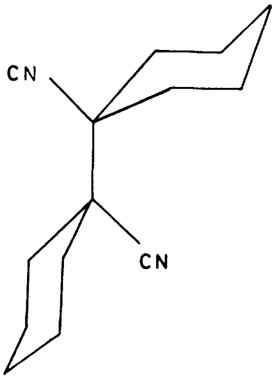


Figure 4. Axial to one ring but equatorial to the other

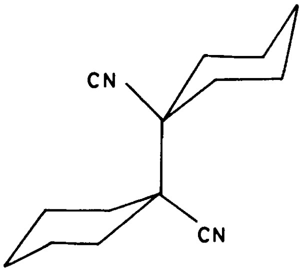


Figure 5. Axial to both rings

Comparison with 2,3-dicyano-2,3-dimethylbutane assuming rigid cyclohexane structures indicates that the disposition of the two carbon atoms of each ring attached to the central carbon atoms of the ethane skeleton are similar to those of the methyl groups in 2,3-dicyano-2,3-dimethylbutane. Consequently, the steric interactions involving the groups attached to the central carbons could be expected to be similar in both molecules. This is borne out by the similarity in the value for dihedral angle as well as for ΔE_s.

Table 6 shows the vibrational species associated with the *trans* conformer. The A_u and B_u types are i.r.-active while the A_g and B_g would give rise to Raman lines. On the other hand, the

Table 6. 1,1′-Dicyanobicyclohexyl: vibrational species

Vibrational species	Activity I.r.	Activity Raman	Total no. of fundamentals	Skeletal	Non-skeletal
trans					
A_g	ia	p*	29	8	21
A_u	a	v	23	5	18
B_g	ia	dp	22	4	18
B_u	a	v	28	7	21
gauche					
A	a	p*	52	13	39
B	a	dp*	50	11	39

gauche rotamer would have 52 *A*-type fundamentals (13 skeletals and 39 non-skeletals) and 50 *B*-type ones (11 skeletals and 39 non-skeletals). All the vibrations are both i.r. and Raman active.

Conformity with the rule of mutual exclusion in the i.r. and Raman spectra [Table 1(b)] suggests that the compound has the *trans* conformation in the solid state.

Extra absorptions of relatively weak intensities observed at 1 530 in C_6H_6, 1 540 in CH_3CN, 950 in $CHCl_3$ and CH_3CN, and 850 cm^{-1} in C_6H_6 and CH_3CN suggest the presence of *gauche* conformers in small proportions in solution. Looking at the ratios of i.r. absorptions for the corresponding pairs of *trans* and *gauche* absorptions, estimates of a *gauche* population of 17 and 23% in C_6H_6 and CH_3CN respectively are deduced. In assigning the vibrational frequencies of the *trans* conformation of the molecule, reference is made to the vibrational frequencies of 2,3-dicyano-2,3-dimethylbutane, cyclohexane,[17] and tetramethylbutane.[28] The frequencies observed in the region 2 800—3 000 cm^{-1} are due to the C–H stretching vibrations with the symmetric C–H stretches found in the region below 2 900 cm^{-1} and the antisymmetric stretches in the region of 2 900—3 000 cm^{-1} for both the i.r. and Raman spectra. The C–N stretching frequency is observed as an intense absorption at 2 240 cm^{-1} in the i.r. spectra and at 2 238 cm^{-1} in the Raman spectrum of the solid state. The bands in the region 1 440—1 470 cm^{-1} are attributed to CH_2 deformations of the cyclohexane rings. The CCH bending modes of cyclohexane appear in the region 1 100—1 400 cm^{-1} and the bands observed in this range for 1,1′-dicyanobicyclohexyl may be similarly assigned. Possible mixing with the C–C stretches as was observed for cyclohexane[17] might be applicable here. The Raman absorption at 1 238 cm^{-1} of tetramethylbutane[28] (TMB) has been assigned to the 55% of central C–C stretch with the rest made up of C–C–C bending (δ CCC) and symmetrical HCH bending (δ HCH) while a similar Raman absorption at 1 238 cm^{-1} was attributed to the central C–C stretch.[3] For 1,1′-dicyanobicyclohexyl the absorptions at 1 035, 1 079, 1 097, and 1 223 cm^{-1} may be due to the C–C stretching frequencies. The Raman band at 951 cm^{-1} has been assigned to the symmetric C–CN stretching and the i.r. absorption at 917 cm^{-1} to the antisymmetrical C–CN stretch.[29] Accordingly, we assign the Raman absorption at 953 cm^{-1} for 1,1′-dicyanobicyclohexyl to a C–CN symmetric stretching vibration. According to the i.r. bands at 933 and 901 cm^{-1}, they are the likely ones for the antisymmetrical stretch.

The frequencies in the region of 600—800 cm^{-1} may be attributed to C–C stretching vibrations with mixing from the angle-bending modes of the ring systems, the Raman band at 648 cm^{-1} or TMB to a mixture of C–C stretches involving the central and non-central carbons.[28] The bands at 668 cm^{-1} observed for 1,1′-dicyanobicyclohexyl might be similarly assigned. The frequencies in the region below 600 cm^{-1} are attributed to the angle-bending modes which involve mainly the carbon atoms of the cyclohexane rings, the CCN and CN–C–CN bending modes.

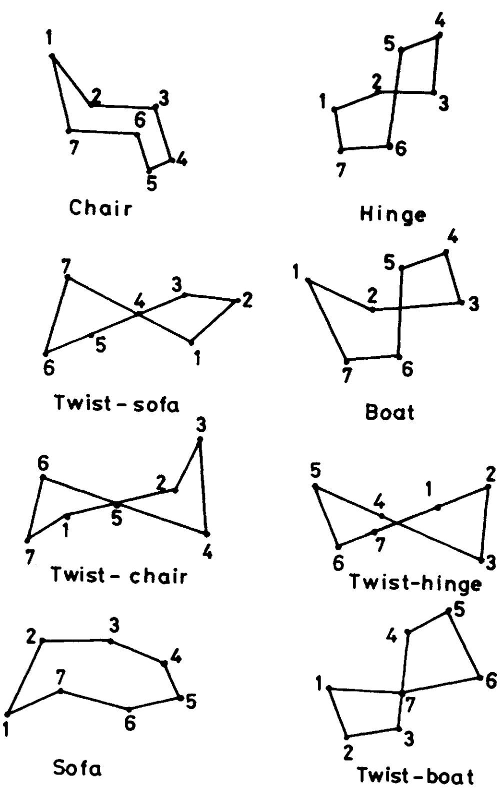


Figure 6. Possible conformations for the cycloheptane ring

Conformers of 1,1′-*Dicyanobicycloheptyl.*—In studying this molecule, one needs first of all to look at the conformations of the seven-membered rings. Although molecular models show that the ring cannot have a rigid structure, yet two factors limit the number of possible configurations (see Figure 6): (a) the mutual repulsions between the links attached to neighbouring carbon atoms and (b) the tendency within the molecule to retain as tetrahedral the C–C–C angles.

Diez *et al.*[30b] have analysed the *X*-ray diffraction data for various compounds containing the seven-membered ring and noted that each of these compounds may be represented by more than one geometry. Calcium cycloheptanecarboxylate pentahydrate for example has as many as four geometries.

In view of the uncertainty in the structure of the seven-membered ring, the molar Kerr constants of 1,1′-dicyanobicycloheptyl corresponding to various 2φ values were not evaluated.

Dipole moment and Kerr constant measurements. Results of dipole moment and Kerr constant measurements are presented in Table 2(c). The Lennard-Jones and Pike plots of the dipole moment data in CCl_4 give a ΔE_s value of 3.1 kJ mol^{-1} and a dihedral angle of 67° corresponding to a *gauche* population of 38%.

An augmentation in electric dipole moment of 2.54×10^{-30} C m was observed for solutions of C_6H_6 as compared with CCl_4 at 25 °C. The value of ΔE_s, the energy difference between the *trans* and *gauche* conformers, calculated for a *gauche* conformer dipole moment of 14.18×10^{-30} C m in C_6H_6 and based on a dihedral angle of 67°, was 1.13 kJ mol^{-1}. The extent of stabilization of the *gauche* conformer by solute–benzene interactions is thus 1.9 kJ mol^{-1}. The large difference in molar

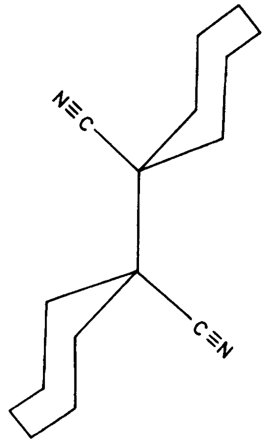
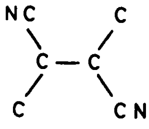


Figure 7. *trans* Conformer of 1,1′-dicyanobicycloheptyl



(1)

Kerr constants in C_6H_6 and CCl_4 of 405 × 10^{-27} C^2 m^5 J^{-2} mol^{-1} is further evidence of the presence of solute–benzene interactions.

It is interesting to note that this is the only molecule in this series of compounds which exhibits curvature in dielectric constant for solutions of both CCl_4 and C_6H_6. Similar deviations from linearity in the plot of $\Delta\varepsilon$ *versus* the weight fraction of solute were recorded for 1,2-dicyanoethane[2] and 2,3-dicyano-2,3-dimethylbutane and indicated the stabilization of the polar form of the molecule by the reaction field of the polar species themselves.

An augmentation in dipole moment was also recorded for the solute in dioxane. Calculation of ΔE_s assuming a dihedral angle of 67° gives a value of 1.3 kJ mol^{-1}. The extent of preferential stabilization of the *gauche* conformer is thus 1.8 kJ mol^{-1}.

For the *trans* conformer (see Figure 7), a σ_h plane of symmetry containing the C–CN bonds and the central C–C bond exists only if the conformation of the seven-membered ring were of the chair, boat, sofa, or hinge forms. Other conformations of the cycloheptane ring would result in a lowering of symmetry of the molecule. Theoretically, these would cause the molecule to lose its centre of symmetry and hence to display the same i.r. and Raman bands. On the other hand most of the ring vibrations are localized and have little effect on the vibrations of (**1**) which may still show an effective centre of symmetry in spite of the cycloheptyl distortions. Such a conformation would give rise to mutually exclusive lines (i.r. and Raman). However, since the i.r. effect is linked intrinsically to the change in dipole moment within a molecule, the disposition of the polar groups would be a more decisive factor in determining the i.r. and Raman bands for a molecule.

For the *gauche* conformer, only a C_2 axis of symmetry exists. This conformer would not display mutually exclusive i.r. and Raman bands, irrespective of the conformation adopted by the seven-membered rings.

The number of fundamental modes corresponding to each vibrational species was worked out by standard methods.[21] The number of atoms in the molecule is 42 and hence the number of fundamentals would be 120 (see Table 7).

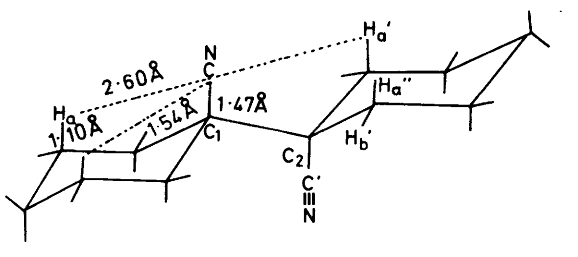


Figure 8. Molecular dimensions of 1,1′-dicyanobicyclohexyl

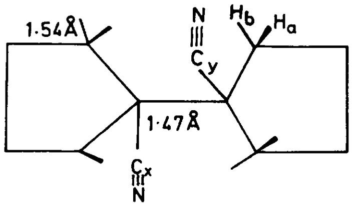


Figure 9. Molecular dimensions of 1,1′-dicyanobicyclopentyl

Table 7. 1,1′-Dicyanobicycloheptyl: vibrational species

Vibrational species	Activity I.r.	Activity Raman	Total no. of fundamentals	Skeletal	Non-skeletal
trans					
A_g	ia	p*	32	8	24
A_u	a	v	29	5	24
B_g	ia	dp	28	4	24
B_u	a	v	31	7	24
gauche					
A	a	p*	61	13	48
B	a	dp*	59	11	48

Examination of the solid-state i.r. and Raman spectra [Table 1(c)] shows that the rule of mutual exclusion is satisfied. We conclude that the compound exists essentially in the *trans*-conformation in the solid state. Extra absorptions in the i.r. spectra at 1 240 in C_6H_6 and CH_3CN, 990 in C_6H_6, 770 in C_6H_6 and CH_3CN, and 675 cm^{-1} in C_6H_6 and CH_3CN suggest the existence of an equilibrium mixture of *gauche* and *trans* conformers in the solution state.

An interesting feature in the solution spectra is the broadening of many absorptions as compared with those in the solid-state spectra. This may be due to either: (a) the presence of bands due to the *gauche* conformers which occur at frequencies very near to the *trans* bands or (b) the presence of continuously distorted cycloheptyl rings in the solution state but of specific conformations of the rings in the solid state. The fact that the absorptions observed in the non-polar solvent CCl_4 are just as diffuse and broadened as those in the polar solvents shows that these additional conformers do not depend on the polarity of the solvents. The broadening of bands in the solution-state spectra could be due to distortions in the seven-membered ring systems.

Comparison of Members of Series.—The equilibrium constant values ($K = N_g/N_t$) in Table 8 show that in CCl_4 solution the *gauche* population increases steadily from *ca.* 4.5 to *ca.* 38% in the series as the ring-size increases. The difference between ΔH° and ΔE [$\Delta H^\circ = \Delta E^\circ + \Delta(PV)$] is negative in the case of 1,1′-dicyanobicyclopentyl and 1,1′-dicyanobicycloheptyl, implying that there is a decrease in volume of the system

Table 8. Thermodynamic quantities governing *gauche–trans* equilibrium in kJ mol^{-1}

Solvent	Temperature (°C)	$K = N_g/N_t$	$\Delta G°$	$\Delta H°$	ΔE
		1,1′-Dicyanobicyclopentyl			
CCl_4	7	0.038	7.61	8.3 ± 0.8	9.28 ± 1.00
	25	0.049	7.47		
	45	0.062	7.35		
Benzene	25	0.151	4.68	3.6 ± 0.2	6.44 ± 0.35
	45	0.165	4.76		
	60	0.175	4.83		
		1,1′-Dicyanobicyclohexyl			
CCl_4	7	0.110	5.14	7.6 ± 1.0	6.60 ± 0.91
	25	0.132	5.02		
	45	0.156	4.91		
Benzene	25	0.234	3.60	4.2 ± 0.5	5.18 ± 0.61
	45	0.253	3.63		
	60	0.277	3.55		
		1,1′-Dicyanobicycloheptyl			
CCl_4	7	0.565	1.33	2.7 ± 0.3	3.05 ± 0.34
	25	0.614	1.21		
	45	0.644	1.16		
		2,3-Dicyano-2,3-dimethylbutane			
CCl_4	7	0.19	3.92	7.4 ± 0.5	5.50 ± 0.42
	25	0.22	3.73		
	45	0.27	3.48		

$\Delta G°$ is calculated from the relation $\Delta G° = -RT\ln K$. $\Delta H°$ is obtained from the slope of the $\ln K$ *versus* $1/T$ plot by the method of least squares and assuming $\Delta H°$ to be constant over the temperature range.

when the more stable *trans* molecules are converted into the *gauche*. In the case of 1,1′-dicyanobicyclohexyl and 2,3-dicyano-2,3-dimethylbutane, the difference is positive suggesting that the process of converting the more stable *trans* into the *gauche* molecules is accompanied by an increase in volume.

Table 8 also shows a steady decrease in ΔE_s from the five- to seven-membered ring systems of this series. This trend was consistently found for all the solvents used in our measurements. These results suggest that differences in internal parameters of each member of the series cause the five-membered ring system to favour the *trans* conformer more markedly than the seven-membered ring system. The behaviour of 2,3-dimethyl-2,3-dicyanobutane is expected to be similar to that of 1,1′-dicyanobicyclohexyl from a steric point of view. The closeness of their respective ΔE_s values supports this expectation. The molecular dimensions of each member are now examined.

Barton models show that the closest non-bonded C(N)–H distances in the *trans* conformer of 1,1′-dicyanobicyclohexyl [indicated by C(N)–$H_{a'}$ and C(N)–$H_{a''}$] are 2.60 Å. The closest C(N)–H distances for the *gauche* conformer with dihedral angle of 60° is still 2.60 Å, whereas it becomes 2.45 Å for a dihedral angle of 85°. If there had not been a contribution from the polar factor, the dihedral angle of the *gauche* conformer would have been 60° and the population of *gauche* conformers 67%. The fact that a very different figure of 11% was obtained together with a dihedral angle of 82° indicates the over-riding effect of the polar factor. The shortest non-bonded C(N)–H distance in 1,1′-dicyanobicyclopentyl in the *trans* conformation is 2.60 Å. However, this becomes 2.30 Å for a dihedral angle of 85°. Although mutual repulsion between the cyanc groups is still the dominant factor as shown by the large dihedral angle of the *gauche* conformer, this conformer is destabilized by an unfavourably short C_x–H_b distance of 2.30 Å, which is shorter than the closest distance of 2.45 Å in the *gauche* conformer of the six-membered ring analogue. This distance would probably result in large van der Waal's repulsions and would explain the higher *gauche* population of 1,1′-dicyanobicyclohexyl compared with its five-membered ring counterpart.

The higher population of *gauche* conformers for 1,1′-dicyanobicycloheptyl suggests that for this molecule, differences in the distances between a cyano carbon atom and non-bonded hydrogen atoms closest to this group in the *trans* and *gauche* conformers are even smaller than those for the six-membered ring analogue.

Acknowledgements

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