Rotational Isomerism in 1,1'-Dinitrobicyclopentyl, 1,1'-Dinitrobicyclohexyl and 1,1'-Dinitrobicycloheptyl

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IR and Raman spectra of 1,1'-dinitrobicyclopentyl, 1,1'-dinitrobicyclohexyl, and 1,1'-dinitrobicycloheptyl in the solid and solution states are reported and assignment of frequencies made. Dipole moments in different solvents (benzene, carbon tetrachloride, and cyclohexane) at different temperatures and molar Kerr constants (in carbon tetrachloride and benzene) are also reported. Analysis of the relative permittivity data shows that, at 25 °C, the compounds in the series exist as rotameric mixtures in carbon tetrachloride solution containing 83, 42, and 16% respectively of the *gauche* rotamer. Benzene causes the *gauche* population to increase, as evidenced by dipole moment and Kerr-constant values in this solvent. The experimentally derived values of the energy difference between *gauche* and *trans* rotamers, the dihedral angle of the *gauche* rotamer, and the *gauche*/*trans* population quotients are compared with values predicted by the semiempirical MO program AMPAC. Comparison of the Raman and IR spectra of the solids suggests that all three compounds exist in the *gauche* conformation in the solid state.

Previous work on 1,1'-dicyanobicyclopentyl, 1,1'-dicyanobicyclohexyl, and 1,1'-dicyanobicycloheptyl[1] revealed that these molecules exist essentially in the *trans* conformation in the solid state but as mixtures of *trans* and *gauche* rotamers in solution. In this paper we report the results of a further study on an analogous series of compounds with the nitro group replacing the cyano group. The obvious difference beween the two series lies in the shape of the polar substituent—the cyano group being cylindrical while the nitro group is triangular. The polarities of the two groups are virtually the same. In addition to relative permittivity, electric birefringence, IR, and Raman spectroscopic measurements, we have also carried out semiempirical molecular orbital (MO) calculations to determine the relative energies, geometries, and relative populations of the *gauche* and *trans* rotamers for comparison with experimental observations.

Experimental

Solutes.—The three dinitrobicyclo compounds were prepared by the method of Seigle and Hass.[2] 1,1'-Dinitrobicyclopentyl had m.p. 79–80 °C (lit.,[3] 80.8–81.3 °C); 1,1'-dinitrobicyclohexyl had m.p. 218–219 °C (lit.,[2] 216–217 °C). *1,1'-Dinitrobicycloheptyl* (m.p. 154–155 °C) has not been reported before. Nitrocycloheptane, required in the preparation, was obtained by adapting the preparation of 2-nitrooctane from 2-bromooctane[4] (Found: C 59.1; H 8.4; N 9.9. $C_{14}H_{24}N_2O_4$ requires C, 59.15; H, 8.45; N, 9.86%).

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 given previously.[5,6]

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 IR spectra were recorded for Nujol and hexachlorobutadiene mulls and for KBr pressed-disc samples. Solution-state spectra were obtained using solvents such as carbon tetrachloride, carbon disulphide, benzene, chloroform, and acetonitrile. A Perkin-Elmer 682 IR spectrophotometer with a spectral resolution of ±4 cm^{-1} and wavenumber accuracy of ±4 cm^{-1} was used for all these IR measurements. Solid- and solution-state Raman measurements were made using the 4 880 Å line of a Spectraphysic argon-ion laser and a JESCO NR1000 spectrometer. The instrument was calibrated with argon emission lines with spectral resolution of ±0.15 cm^{-1}.

Semiempirical molecular orbital calculations were performed using the program AMPAC.[10] AM1 parametrization[11] was used. Full geometry optimization and fixed-geometry calculations were performed for each incremental value of the ethane C–C torsion angle. Torsion or dihedral angles were defined by the atoms N–C–C–N by the convention of Klyne and Prelog.[12] Calculations were performed on a Silicon Graphics Personal Iris computer using Fortran 77 operating under UNIX.

Results and Discussion

The more relevant spectroscopic results are given in Table 1; the results of the other physical measurements are presented in Table 2 with standard notation.

Conformers of 1,1'-*Dinitrobicyclopentyl.*—Fig. 1 shows the various conformations of the cyclopentane ring which have been proposed.[13–19] Conformation (*a*), with four carbon atoms in one plane, is known as the 'envelope form' with C_s symmetry. In conformation (*b*), three adjacent carbon atoms lie in the same plane. Conformation (*c*) is a structure proposed by LeFevre.[13] It is a C_2 half-chair form with three adjacent carbon atoms twisted so that one is as much above the plane as the other is below. This structure is a special case of conformation (*b*).

According to Kilpatrick *et al.*,[14] none of these forms, as well as a multitude of other intermediate types, differ much in energy. However, LeFevre[13] has shown by polarizability measurements that while a C_s cyclopentane structure did not fit their data, the C_2 form gave a good fit. McCullough,[20] through his work on the vapour heat capacity of cyclopentane, demonstrated that only if cyclopentane is assumed to undergo pseudorotation can experimental and calculated entropy and vapour heat capacity data be reconciled. This would mean that no single,

Table 1(*a*). Vibrational spectra of 1,1′-dinitrobicyclopentyl

IR			Raman				
KBr	CCl_4 2.5%	MeCN 3.4%		CCl_4	MeCN	Approximate group assignment	
ε_{20} =	2.238	37.5	Solid	6.5%	22.3%		
2 960(55)	2 960(76.5)	X	2 970(100)	2 980(58)	X	ν_{CH}(asym)	
2 882(28.5)	2 880(33)	X	2 875(52.5)	2 890(34)	X	ν_{CH}(sym)	
1 550(72)	1 555(22)	X	1 550(28)	1 550(69)	X	ν_{NO_2}(asym)	
1 542(10)	1 545(2)	X	1 540(33)	1 535(68)		δ_{CH_2}(ring)	
1 475(36.5)	1 470(7.5)	X	1 470(26.5)	1 475(23)			
1 458(43.5)	1 451(37)	X	1 450(66)	1 455(35)			
1 365(71)	1 350(50)	X	1 360(92.5)	1 360(53)	X	ν_{NO_2}(sym)	δ_{CCH}
				1 350(51)	X		
1 338(24.5)	1 325(5)	X	1 330(32)	1 330(29)	1 325(22)		
1 319(45)	1 315(19)	X	1 310(23)			τ_{CH_2}(wag)	
1 194(28.5)	1 188(32)	1 190(28)	1 187(78)	1 190(15)	1 175(13)	ν_{C-C}	
	1 125(9)	1 125(10)	1 135(21)	1 120(16)			
1 060(14)	1 045(18)	X	1 050(26)	1 045(30)	X		
955(13)	943(33.5)	947(30)	955(15.5)	950(20)			
911(16.75)	907(18.25)	900(4.5)	913(79)	912(80)		ρ_{CH_2}	
852(61)	845(65)	850(75)	857(30.5)	X	840(27)	$\nu_{CN}(c_2)$	
837(2)			837(55)	X	825(30)		
665(26)	661(21)	655(22)	662(18)	650(27)	645(7)	ρ_{NO_2}	
				532(4)	522(10)	δ_{ring}	
	475(17.75)	479(15.75)	463(22)	X	482(21)		
427(11)	430(1.5)	432(3)	427(37)	X	455(20)		

Table 1(*b*). Vibrational spectra of 1,1′-dinitrobicyclohexyl

IR			Raman				
KBr	CCl_4 0.61%	MeCN 0.91%	Solid	CCl_4 0.60%	MeCN 5.16%	Approximate group assignment	
	2 990(6)	X[a]	3 005(38)	2 991(8)	X	ν_{CH}(asym)	
2 955(56)	2 955(66)	X	2 950(75)	2 948(36)	X		
	2 865(2)	X[b]	2 875(62.5)	2 874(9)	X	ν_{CH}(sym)	
1 568(4)	X	X	1 542(27.5)	1 540(7)	X	ν_{NO_2}(asym)	
1 455(40)	1 453(57.5)	X	1 450(53.5)		X	δ_{CH_2}(ring)	
1 432(48)	1 429(16)	X	1 430(27)	1 428(8)	X		
1 341(24.5)	1 341(51)	X	1 342(23)	1 340(11)	X	ν_{NO_2}(sym)	δ_{CCH}
1 311(3.5)	1 310 sh(1.5)	X	1 305(20.5)				
1 254(4.5)	1 250(3)	1 258(11)	1 255(23.5)	1 261(7)	1 250(31)		
	1 130(13)	1 129(2)	1 135(31)	1 140(5)	1 135(19)	ν_{CC}	
1 089(6.5)	1 084(3)	X	1 085(24)	1 099(12)			
1 075(13)	1 070(1)	X					
1 044(16)	1 033(3.5)	X	1 040(55)				
1 022(11)	1 017(23.5)	X		1 029(11)			
947(10)	943(1.5)	942(4)	942(12)		X		
845(49)	840(34)	845(46)	840(26)	X	840(25)	ν_{CN}	
	X[c]	820(1)	835(16)	X	835(25)	ν_{CC} & δ_{ring}	
648(6)	X	642(3)				ρ_{NO_2}	
543(24)	536(19.5)	535(7)	535(38)	535(9)	537(15)	δ_{ring}	
518(28.5)	513(6)	513(9)	512(41)	507(12)	512(15)		
465(5)	465(11)	465(2)					

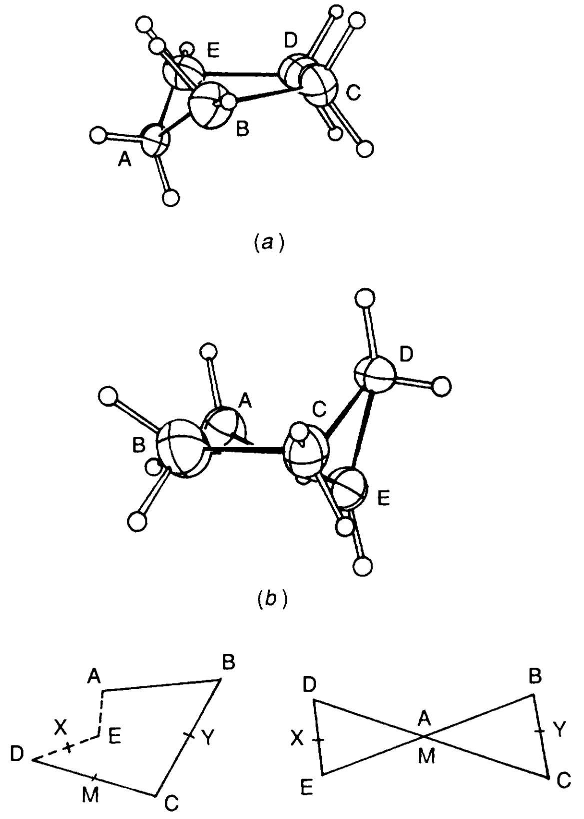
[a] In $CHCl_3$ (ε_{20} 4.806, conc. 1.5%), the band at 2 985 cm^{-1} has an intensity of 2%. [b] In $CHCl_3$, the band at 2 860 cm^{-1} appears as a shoulder. [c] In CS_2 (ε_{20} 2.641, conc. 0.78%), the band at 819 cm^{-1} has an intensity of 4%.

unambiguous structure will suffice for cyclopentane itself. However, for 1,1′-dinitrobicyclopentyl in the solid state, a recent X-ray crystal diffraction study[21] has shown that the compound adopts the *gauche* conformation and that the cyclopentyl ring is non-planar, irregular, and puckered such that only three adjacent carbon atoms are in the same plane [similar to conformation (*b*)]. However, the situation could be different when the compound is in solution where greater flexibility involving pseudorotation of the cyclopentyl rings can be expected.

Spectroscopy. For this compound, we assume that a σ_h plane exists in the *trans* form which bisects the cyclopentyl ring. This would also be true if the cyclopentyl rings were to undergo constant pseudorotation in solution. The *gauche* conformer possesses only a C_2 axis of symmetry, which bisects the torsion

Table 1(*c*). Vibrational spectra of 1,1′-dinitrobicycloheptyl

IR			Raman			Approximate group assignment
KBr	CCl_4 2.0%	MeCN 2.9%	Solid	CCl_4 16.1%	MeCN 5.0%	
2 940(73.25)	2 930br(60)	X	2 940(100)	2 960(87)	X	ν_{CH}(asym)
2 875(31.25)	2 860(24.25)	2 855(60)	2 850(51)	2 870(61)	X	ν_{CH}(sym)
	2 810(3)					
1 550(78)	1 550(40)	X	1 535(24.5)	1 545(50.5)	X	ν_{NO_2}(asym)
1 463(15)	1 462(40)	X		1 462(19)	X	
1 431(43)		X	1 440(48)	1 447(38)	X	δ_{CH_2}(ring)
1 358(42.5)	1 360(43)	X	1 365(9)	1 370(18.5)	X	ν_{NO_2}(sym)
1 302(28.5)	1 288(4.75)	1 290(18)	1 292(22)	1 295(20)	1 305(21)	τ_{CH_2}(wag)
1 195(12.75)	1 182(2.75)	1 191(3.25)	1 180(6)	1 185(13.5)		δ_{CCH}
1 150(18.25)	1 162(20)	1 164(8)	1 160(3)	1 160(14)	1 165(31)	
	1 142(7.25)	1 145(7.25)				
1 077(6.5)	1 085(9)	1 085(14.75)	1 085(12.5)	1 085(28)		ν_{CC}
1 013(26)	1 006(1.5)	X	1 015(8)	1 020(20)	X	
	959(40)	958(54)	950(1.5)		945(28)	
860(47)	849(54.5)	853(73.5)	865sh	857(4)	855(23)	ν_{CN}
823(23)	X	823(29.5)	830(16)	X	827(18)	
635(12)	638(2.75)	640(10.75)				ν_{CC} & δ_{ring}
	597(25)	599(15)	600(10)	600(24)	615(23)	ρ_{NO_2}
515(30.5)	515(8)	510(6)	520(13)		515(45)	
	483(4.75)	485(3)				
458(15)	458(1.5)	455(4)	460(6)		455(56)	δ_{ring}
	440(21)	440(10)				



X, M, and Y are the mid-points of DE, CD, and BC respectively such that A, X, M, and Y lie on one plane.

(*c*)

Fig. 1 Possible conformations of the cyclopentane ring.

angle formed by the two C–NO_2 bonds. The vibrational species of the fundamental modes are given in Table 3.[22]

In making spectral assignments, we have taken advantage of our earlier studies on 2,3-dimethyl-2,3-dinitrobutane[23] and 1,1′-dicyanobicyclopentyl[1] as well as the work of Miller and Inskeep[24] on cyclopentane. The frequencies observed in the region 2 880–3 000 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 2 900–3 000 cm^{-1} for both the IR and the Raman spectra. The C–NO_2 stretching modes are known to give rise to intense absorption in the 1 560–1 340 cm^{-1} region.[25] Similarly, the bands at 1 550 and 1 365 cm^{-1} of the IR spectrum and at 1 550 and 1 360 cm^{-1} of the Raman spectrum are assigned to the respective antisymmetric and symmetric stretching vibrations of the NO_2 group. The two relatively strong bands at 857 and 837 cm^{-1} in the solid Raman spectrum and at 852 cm^{-1} of the KBr pressed disc spectrum are assigned to the CN stretching vibrations (in C–NO_2). This assignment is reasonable since these bands do not appear in the spectrum of the cyano analogue of this compound where the C–NO_2 vibrations do not exist. The bands at 662 cm^{-1} of both the IR and Raman spectra have been assigned to the bending mode of the nitro group. This assignment is tentative since the frequencies in this region may also be attributed to C–C stretching vibrations with mixing from the angle-bending modes of the ring systems. The frequencies in the region below 600 cm^{-1} are attributed to the angle-bending modes of the carbon atoms of the cyclopentyl rings.

Comparison of the IR and Raman spectra of the compound in the solid state shows that many absorption bands coincide in frequency. This is evidence of the absence of a centre of symmetry in the conformation(s) of the compound in the solid state. However, the presence of two extra IR bands at 475 and 1 125 cm^{-1} and two extra Raman bands at 1 350 and 532 cm^{-1} of the solution-state spectra suggests strongly that at least two rotamers are present in solution. However, unlike many of the compounds studied earlier, these bands do not show significant changes in intensity as the polarity of the solvent increases. This suggests that one of the rotamers may be present in unusually high proportion such that the *gauche* : *trans* ratio is found not to vary significantly with the polarity of the solvent. However,

Table 2 Molar polarizations, refractions, dipole moments, and molar Kerr constants at infinite dilution of 1,1′-dinitrobicylopentyl, 1,1′-dinitrobicyclohexyl, and 1,1′-dinitrobicycloheptyl. 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 $\alpha\varepsilon_1 = \Sigma\Delta\varepsilon/\Sigma w_2$, $\beta d_1 = \Sigma\Delta d/\Sigma w_2$, $\gamma n_1{}^2 = \Sigma\Delta n^2/\Sigma w_2$, $\delta B_1 = \Sigma\Delta B/\Sigma w_2$. When the plots of $\Delta\varepsilon$ *versus* w_2 showed curvature, 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 $\alpha\varepsilon_1 = a{\cdot}_{\infty}(\mathrm{m}K_2)$ refers to the solute molar Kerr constant at infinite dilution.

T/°C	Solvent	Conc. range ($10^5\ w_2$)	$\alpha\varepsilon_1$	β	γ	δ	P_2/cm^3	R_D/cm^3	$\mu^a 10^{-30}$ C m	$mK_2/10^{-27}$ m^5 V^{-2} mol^{-1}
(*a*) (*i*) 1,1′-Dinitrobicyclopentyl (R_D = 55.5 cal)										
5	CCl_4	556–1 500	25.64	−0.243			651.2		17.38 ± 0.07	
25	CCl_4	440–1 510	22.52	−0.257	0.065	−16.51	597.1	56.4	17.08 ± 0.03	−59 ± 2
45	CCl_4	780–1 685	19.26	−0.189			536.1		16.61 ± 0.13	
7	C_6H_6	530–880	16.97	0.275			756.5		18.92 ± 0.10	
25	C_6H_6	485–825	15.13	0.319	0.015	−19.98	701.9	54.5	18.74 ± 0.03	−502 ± 6
45	C_6H_6	420–760	13.25	0.325			645.9		18.49 ± 0.13	
25	C_6H_{12}	170–825	9.28	0.381			554.4	56.5	16.41 ± 0.03	
(*ii*) Nitrocyclopentane (R_D = 28.8 cal)										
25	C_6H_6	1 000–5 800	12.03	0.209	−0.071		292.5	29.2	11.94 ± 0.03	
(*b*) (*i*) 1,1′-Dinitrobicyclohexyl (R_D = 64.8 cal)										
5	CCl_4	185–255	8.25	−0.255			275.0		10.27 ± 0.13	
25	CCl_4	165–260	7.93	−0.238	0.081	63.19	273.5	64.6	10.58 ± 0.17	−23 ± 4
45	CCl_4	180–370	7.54	−0.272			273.8		10.94 ± 0.13	
25	C_6H_6	700–2 100	7.88	0.302	0.016	−7.99	440.6	63.5	14.24 ± 0.07	−237 ± 32
45	C_6H_6	670–2 100	7.03	0.324			412.9		14.14 ± 0.10	
60	C_6H_6	370–1 900	6.30	0.316			388.0		13.98 ± 0.10	
25	C_6H_{12}	60–165	3.25	0.401			250.2	64.5	9.97 ± 0.53	
(*ii*) Nitrocyclohexane (R_D = 33.4 cal)										
25	C_6H_6	520–3 700	11.48	0.181	−0.069		315.0	32.9	12.34 ± 0.05	
(*c*) 1,1′-Dinitrobicycloheptyl (R_D = 74.0 cal)										
5	CCl_4	440–670	3.65	−0.337			174.9		7.04 ± 0.10	
25	CCl_4	345–750	3.97	−0.292	0.078	16.52	186.9	74.0	7.71 ± 0.17	45 ± 2
45	CCl_4	580–930	3.98	−0.286			192.5		8.14 ± 0.07	
7	C_6H_6	520–790	3.88	0.328			264.2		9.80 ± 0.09	
25	C_6H_6	730–5 510	3.54	0.283	0.019	−6.10	258.6	72.9	9.94 ± 0.03	−169 ± 4
45	C_6H_6	550–760	3.50	0.362			257.2		10.25 ± 0.10	
25	C_6H_{12}	285–645	1.75	0.329			181.9	74.8	7.64 ± 0.10	

^{a} ${}_DP = 1.05R_D$.

Table 3 Vibrational species of 1,1′-dinitrobicyclopentyl **1**, 1,1′-dinitrobicyclohexyl **2**, and 1,1′-dinitrobicycloheptyl **3**.

		Activity		1			2			3		
Point group	Vibrational species	IR	Raman	Non-skeletal	Skeletal	Total No. fundamentals	Non-skeletal	Skeletal	Total No. fundamentals	Non-skeletal	Skeletal	Total No. fundamentals
C_{2h}	A_g	ia	p*	15	9	24	21	9	30	24	9	33
	A_u	a	v	15	7	22	18	7	25	24	7	31
	B_g	ia	dp	15	6	21	18	6	24	24	6	30
	B_u	a	v	15	8	23	21	8	29	24	8	32
C_2	A	a	p*	30	16	46	39	16	55	48	16	64
	B	a	dp*	30	14	44	39	14	53	48	14	62

relative to the intensities of (say) the 655 cm^{-1} IR absorption, the intensity of the 475 cm^{-1} band decreases slightly in the strongly polar solvent MeCN. As polar solvents are known to favour the more polar *gauche* rotamer this suggests that the 475 cm^{-1} absorption could be a *trans* band. All these observations are consistent with the existence of the compound in the *gauche* conformation in the solid state[21] but as a mixture of *gauche* and *trans* rotamers in solution with the *gauche* predominating even in non-polar solvents.

Dipole moment and Kerr effect measurements. The dipole moment of nitrocyclopentane, being needed in the calculations for the dipole moment of the different conformations of 1,1′-dinitrobicyclopentyl, has also been measured in benzene at 25 °C and the results are included in Table 2(*a*).

The non-planar model of the cyclopentyl ring proposed by LeFevre[13] was adopted for the calculation of the dipole moments and Kerr constants of the various conformations of 1,1′-dinitrobicyclopentyl. The method of calculation is similar

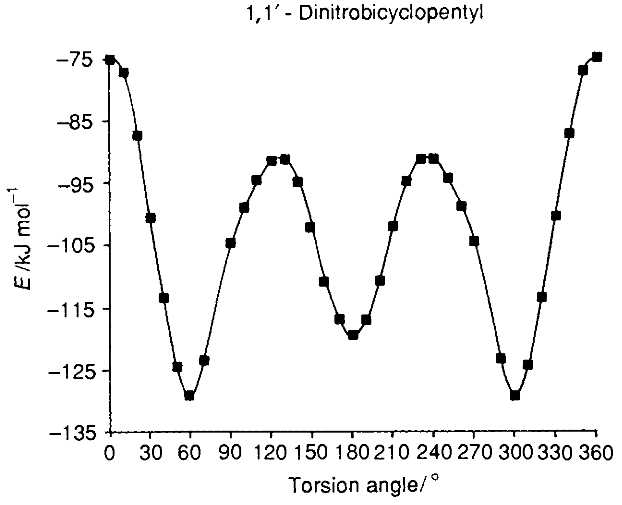


Fig. 2 Energy of 1,1'-dinitrobicyclopentyl as a function of the N–C–C–N angle

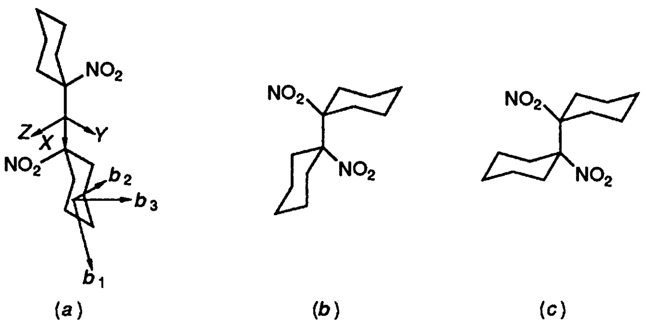
to that used for 2,3-dimethyl-2,3-dinitrobutane with the required polarizability values given in Table 4. However, all the calculated m*K*-values for the different conformations were found to be positive while the observed experimental m*K*-value in carbon tetrachloride is negative. Therefore, it seems unlikely that the cyclopentyl rings in 1,1'-dinitrobicyclopentyl will have conformation (*c*) in solution.

AMPAC calculations with AM1 parametrization and allowing full geometry optimization gave values for ΔE, torsion angle of the *gauche* rotamer, and % *gauche* population (Fig. 2) which compare well with those determined experimentally for carbon tetrachloride solution (Table 5).

Table 4 Anisotropic polarizabilities of bonds and groups expressed as 10^{-40} C^2 m^2 J^{-1}

Bond-group	b_L	b_T	b_V	Ref.
C–C	1.09	0.29	0.29	13(*a*)
C–NO$_2$	3.78	3.12	2.56	28
b_i'[a] (cyclopentyl)	9.26	8.47	7.61	29
b_i''[b] (cyclohexyl)	10.91	10.91	9.35	13(*a*)

[a] b_i' = Group polarizability of cyclopentyl (C_5H_9) based on the cyclopentane model adopted. [b] b_i'' = Group polarizability of cyclohexyl (C_6H_{11}) based on the cyclohexane model adopted.



(*a*) (*b*) (*c*)

Fig. 3 Possible *trans* conformers of 1,1'-dinitrobicyclohexyl

The corresponding results for benzene solution are −5.81 kJ mol^{-1} for ΔE, 47° for the torsion angle, and 84% for the *gauche* population. The smaller torsion angle may be the result of distortion caused by solute/benzene interaction.

Conformers of 1,1'-*Dinitrobicyclohexyl*.—Our X-ray diffraction study[21] of 1,1'-dinitrobicyclohexyl has shown that the molecule exists in the *gauche* conformation in the solid state with the cyclohexyl rings adopting the chair form (D_{3h} symmetry) rather than any of the other conformations which the cyclohexane ring can assume. Fig. 3 shows the possible conformations of the *trans* conformer of 1,1'-dinitrobicyclohexyl. 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. The *gauche* rotamer has only a C_2 rotational axis and thus belongs to the C_2 point group.

Spectroscopy. Table 3 gives the vibrational species associated with the *trans* and *gauche* conformers. For the C_{2h} form, 54 fundamentals are due to the A_u and B_u modes and are IR active while the rest are Raman active. The *gauche* rotamer, having no centre of symmetry, would have twice as many absorptions in the IR spectrum as the *trans*, as all its fundamental modes are both IR and Raman active. However, the internal vibrations of the CH_2 groups would prevent a certain number of bands from being observed in both rotamers, because of considerable overlapping and masking.

Inspection of the Raman and IR spectra in the solid state reveals that the frequencies at which the bands occur are not

Table 5 Comparison between 1,1'-dinitro and 1,1'-dicyano bicycloalkanes

	ΔE^+/kJ mol^{-1}		Torsion angle of *gauche* rotamer/°		% *gauche* population		Barrier height/kJ mol^{-1} between *gauche* and *trans* forms
Compound	Experimental[d]	AM1	Experimental	AM1	Experimental	AM1	AM1
1,1'-Dicyanobicyclopentyl[a]	−2.25	−1.69	67	58	83	80	21.82
1,1'-Dicyanobicyclohexyl[b]	2.59	1.44	90	59	42	53	32.68
1,1'-Dicyanobicycloheptyl[b]	5.99	5.82	64	57	16	16	49.92
	Experimental	MMP2	Experimental	MMP2	Experimental	MMP2	MMP2
1,1'-Dinitrobicyclopentyl[c]	9.28	10.71	85	61	4.5	2.5	22.34
1,1'-Dinitrobicyclohexyl[c]	6.60	11.17	86	60	11	2	27.48
1,1'-Dinitrobicycloheptyl[c]	3.05	3.51	67	52	38	33	30.25

[a] AM1 calculations with full geometry optimization. [b] AM1 calculations using fixed geometries. [c] MMP2 calculations with full geometry optimization. [d] Experimental values are based on the Lennard-Jones–Pike method of calculation using data from measurements on CCl_4 solutions. ΔE^+ is defined as E(*gauche*) − E(*trans*).

Table 6 Calculated dipole moments and molar Kerr constants with corresponding percentage population for various conformations of 1,1′-dinitrobicyclohexyl, based on data in benzene

Dihedral angle/°	$\mu_{calc}/10^{-30}$C m	x (%)	m$K_{calc}/10^{-27}$ m^5 V^{-2} mol^{-1}	x (%)
0	23.19	20.8	−804.3	3.0
60	20.09	27.7	−348.5	7.0
70	19.02	31.0	−239.2	10.2
80	17.79	35.4	−141.4	17.2
90	16.42	41.6	−61.5	39.1
93	15.99	44.2	−41.8	57.0
100	14.92	50.3	−2.3	749.2
180	0		1.0	

mutually exclusive. This indicates that, in the solid state, the compound exists in a conformation which does not possess a centre of symmetry. However, in the IR spectra in the solution states, a few extra bands at 820, 1 129, 2 865, and 2 990 cm^{-1} are observed and these bands are found to decrease in intensity with increasing polarity of the solvents. In fact, these extra bands are extremely weak in the polar acetonitrile solution. They are therefore attributed to the *trans* rotamer and their existence leads to the conclusion that only the *gauche* form is present in the solid state. This situation is very similar to that in 2,3-dimethyl-2,3-dinitrobutane where the extra bands in solution are attributed to the *trans* rotamer and the solid state is found to consist only of the *gauche* rotamer. The very weak intensities of the bands attributed to the *trans* rotamer in acetonitrile indicates that only a very small proportion of this rotamer is present in this very polar solvent. However, the proportion of *trans* rotamer in carbon tetrachloride and carbon disulphide is higher than in acetonitrile, indicating that the *trans* population decreases as the polarity of the solvent increases.

Although all the bands of the solid are attributed to the *gauche* rotamer, it is interesting to note that many of the bands increase in intensity in carbon tetrachloride solution. This is probably due to the fact that the bands due to the *trans* rotamer (which comes into existence in solution) coincide with the *gauche* bands, causing a resultant increase in the intensities. Such bands are found at 465, 1 022, 1 341, 1 453, and 2 955 cm^{-1}. This increase in intensity is quite substantial in many cases. In addition, inversion of intensities between neighbouring bands is observed in a few cases. Bands in the solid-state spectra at 543 (weaker) and 518 (stronger), 1 044 (stronger) and 1 023 (weaker) and 1 089 (weaker) and 1 075 cm^{-1} (stronger) have their relative intensities reversed in non-polar solvents.

Thus the IR and Raman data are consistent with the conclusion that the stable rotamer in the solid state is the *gauche* form while a mixture of *gauche* and *trans* rotamers exists in solution. The proportion of the *trans* rotamer in carbon tetrachloride is quite high, probably higher than the *gauche* form as evidenced by the intensities of the bands. However, the proportion of the *trans* rotamer decreases with increasing polarity of the solvents and becomes rather small in the very polar acetonitrile solution.

Thus 1,1′-dinitrobicyclohexyl behaves very much like 2,3-dimethyl-2,3-dinitrobutane. This shows that replacement of the four methyl groups by two cyclohexane ring systems does not affect the behaviour of the compound as far as rotational isomerism is concerned. The cyclohexane rings are quite rigid and the disposition of the C-2 and C-6 carbon atoms of the ring and the hydrogen atoms attached to them are similar to those of the methyl groups in 2,3-dimethyl-2,3-dinitrobutane. Consequently, the steric interactions involving the groups attached to the central carbons would be expected to be similar in both molecules. The other three methylene groups on each cyclohexane ring are too far away from the nitro groups to affect rotation about the central C–C bond.

Dipole moment and Kerr effect measurements. The dipole moment of nitrocyclohexane, being needed in the calculations for the dipole moment of the different conformations of 1,1′-dinitrobicyclohexyl, has also been measured in benzene at 25 °C. Results are included in Table 2(b).

We have calculated the percentage of *gauche* conformer for various dihedral angles and the corresponding dipole moments and Kerr constants for these conformations. The Kerr constants were calculated using the bond and group polarizabilities summarized in Table 4. The molecular polarizabilities of cyclohexane[13a] have been found to be $b_1 = b_2 = 12.30 \times 10^{-40}$ C^2 m^2 J^{-1} and b_3 10.74 × 10^{-40} C^2 m^2 J^{-1}, with b_1 and b_2 in the plane made by the carbon atoms 1, 3, and 5 or 2, 4, and 6 of the cyclohexane ring, and b_3 being perpendicular to this plane. In our calculations the cartesian axes are chosen such that b_1, b_2, and the Y-axis are in the same plane [as shown in Fig. 3(*a*)]. The components of polarizabilities of the cyclohexyl group are given by: b_1(cyclohexane) − $2b_1$(C–H) whence $b_1 = b_2 = 10.86 \times 10^{-40}$ C^2 m^2 J^{-1} and $b_3 = 9.30 \times 10^{-40}$ C^2 m^2 J^{-1}. The results of the calculations for the dipole moments and Kerr constants of the various conformations are set out in Table 6. The dipole moment of the symmetrical half of the molecule (μ_0) is taken to be that of nitrocyclohexane in the direction of the C–N bond of the C–NO$_2$ group.

When the calculated values of percentage *gauche* rotamer are plotted against the dihedral angle, it is seen that the observed dipole moment of 10.58 × 10^{-30} C m and the molar Kerr constant of −23 × 10^{-27} m^5 V^{-2} mol^{-1} in carbon tetrachloride solution are compatible with a mixture containing 42% of the *gauche* rotamer with a dihedral angle of 91°. Substituting these values into Boltzmann's equation gives a value of 2.47 kJ mol^{-1} for ΔE. The alternative Lennard-Jones and Pike[26] approach gave 2.59 kJ mol^{-1} for ΔE, 16.35 × 10^{-30} C m for μ_g, 90° for the dihedral angle of the *gauche* rotamer, and 42% for the *gauche* population. The two sets of results are consistent with each other and substantiate in more precise terms our spectroscopic data which indicate that, in non-polar solvents like carbon disulphide and carbon tetrachloride, the proportion of *trans* rotamer present is probably higher than that of the *gauche* form.

These values compare well (see Table 5) with those AM1 results obtained by assuming a chair geometry for the cyclohexyl rings and fixed orientations for the NO$_2$ groups such that the NCC plane containing the central carbon atoms and the ONC plane are perpendicular to each other; and a fixed bond length of 1.579 Å for the central C–C bond as disclosed by our X-ray study.[21] The predictions from a full geometry optimization calculation, however, agreed poorly with the experimental results.

For benzene solution the Lennard-Jones and Pike analysis gave −1.23 kJ mol^{-1} for ΔE, 16.28 × 10^{-30} C m for μ_g, 91° for the torsion angle of the *gauche* rotamer, and 77% for the *gauche* population.

Conformers of 1,1′-*Dinitrobicycloheptyl*.—Fig. 4 shows the possible conformations of a cycloheptane ring.[27]

However, an X-ray study[21] has shown that the title compound exists in the *gauche* conformation in the solid state with the cycloheptyl rings in the chair conformation. This chair conformation, however, may not necessarily persist in solution where greater flexibility in behaviour is possible.

Spectroscopy. For 1,1′-dinitrobicycloheptyl in solution, we assume that the two cycloheptane rings are in the chair conformation. The *trans* rotamer would belong to the C_{2h} point group while the *gauche* rotamer is of C_2 point group. The vibrational species of the fundamental modes are summarized in

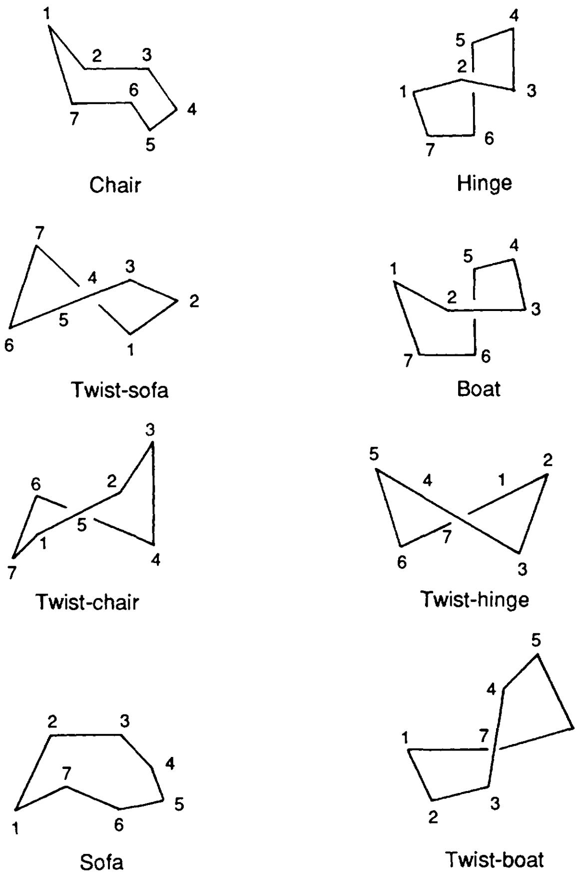


Fig. 4 Possible conformations for the cycloheptane ring

Table 3. For the C_{2h} form, 63 of the fundamental modes are associated with classes A_u and B_u and are IR active. The remaining modes are Raman active. On the other hand, all the absorptions in the C_2 form are both IR and Raman active.

Comparison of the IR and Raman spectra [Table 1(c)] of the compound in the solid state shows that all the Raman lines coincide with some of the IR bands. This is consistent with the *gauche* conformation of the molecule in the solid state. However, several extra IR bands at 2 810, 1 142, 959, 597, 483, and 440 cm^{-1} and an extra Raman band at 1 462 cm^{-1} are found in the spectra of the compound in solution as compared with those in the solid. These bands are found to decrease in intensity with increasing polarity of the solvent and can therefore be attributed to the non-polar *trans* rotamer. In addition the intensities of such bands at 440 and 597 cm^{-1} also suggest strongly that the *trans* rotamer is present in rather high proportion in carbon tetrachloride and carbon disulphide.

Many bands present in the solid-state spectra are also observed to decrease in intensity on dissolution in non-polar solvents. Such bands are at 458, 515, 635, 1 013, 1 077, and 1 302 cm^{-1}. The decrease in intensity of these bands is found to be quite appreciable and this could be due to the presence of a substantial amount of the *trans* rotamer in the solution state.

Hence, from the IR and Raman spectra of the compound, we can conclude that 1,1′-dinitrobicycloheptyl exists exclusively in the *gauche* form in the solid state, while in solution a mixture of *gauche* and *trans* rotamers is present with the *trans* form being present in rather high proportion, especially in non-polar solvents.

Another interesting feature of the solution spectra is the shift in frequency of a number of absorption bands as compared with those in the solid state. Bands at 1 077, 1 150, 1 195, and 1 302 cm^{-1} are shifted to 1 085, 1 162, 1 182, and 1 288 cm^{-1} respectively. In addition, the absorption band at 2 940 cm^{-1} also becomes broader on dissolution as compared with that in the solid-state spectra. This may be due to the presence of continuously distorted cycloheptyl rings in the solution state, whereas in the solid state the cycloheptyl rings adopt a rigid chair conformation.

Dipole moment and Kerr effect measurements. The dipole moment of the compound in carbon tetrachloride at 25 °C is rather low, indicating the presence of a large percentage of the *trans* rotamer. This result is in agreement with our spectroscopic data.

Analysis of our dipole moment data in carbon tetrachloride solution according to the Lennard-Jones–Pike method gives values of ΔE, dihedral angle, and % *gauche* population which are in satisfactory agreement (see Table 5) with those predicted by AM1 calculations based on a fixed geometry (wherein the cycloheptyl rings are assumed to have the chair conformation, the nitro groups to have a fixed orientation such that the NCC plane containing the central carbon atoms and the ONC plane are perpendicular to each other, and the central C–C bond length to have a value of 1.601 Å as shown by our X-ray study.)[21] However, they agree poorly with those predicted by a full geometry-optimized calculation.

Application of the Lennard-Jones–Pike method to the dipole moment data in benzene gives a ΔE-value of 3.32 kJ mol^{-1} with the dipole moment of the *gauche* rotamer equal to 17.03×10^{-30} C m, torsion angle of 84°, and a *gauche* content of 34%.

Comparison of Members of Series.—Table 7 shows the free energy and enthalpy values for the *trans*/*gauche* equilibrium of the three compounds. In carbon tetrachloride in which no specific solute–solvent interactions are expected, the difference between $\Delta H°$ and ΔE [$\Delta H° = \Delta E + \Delta(PV)$] is negative for all three solutes, implying that the process of converting the *trans* into the *gauche* molecules is accompanied by a decrease in volume, in spite of a change in ring size. This decrease in volume suggests that the steric requirements of the *gauche* rotamer are smaller than those of the *trans*. On the other hand, in benzene solution, the difference between $\Delta H°$ and ΔE is negative only in the case of 1,1′-dinitrobicyclohexyl and 1,1′-dinitrobicycloheptyl. However, since the magnitude of the difference is similar to that in carbon tetrachloride, it would appear that intermolecular interactions between the solute and benzene solvent molecules have little effect on the overall change in the volume when the *trans* rotamers are converted into the *gauche* in these two compounds. In the case of 1,1′-dinitrobicyclopentyl, the difference is positive, suggesting that the process of conversion from the *trans* into the *gauche* molecules is accompanied by an increase in volume.

Comparison between 1,1′-Dinitro- and 1,1′-Dicyano-bicycloalkanes in Solution.—The differences in rotational isomeric behaviour between the 1,1′-dinitrobicycloalkanes and the 1,1′-dicyanobicycloalkanes are brought out clearly in Table 5. In the dinitro series, a steady increase in the magnitude of ΔE is observed from the five- to the seven-membered-ring compounds, reflecting the decrease of the *gauche* population from 83 to 16% as ring size increases. In the dicyano series the opposite trend is observed with the ΔE-value decreasing and the *gauche* population increasing from 4.5 to 38% as ring size increases.

Although AM1 calculations gave results which were in satisfactory agreement with experiment in the nitro series this was not the case in the dicyano series. We therefore carried out molecular mechanics (MMP2 programme[30,31]) calculations as an alternative approach which, as Table 5 shows, gave good predictions in the case of 1,1′-dicyanobicyclopentyl and 1,1′-dicyanobicycloheptyl, but was less successful with 1,1′-dicyano-

Table 7. Thermodynamic quantities governing *gauche–trans* equilibrium in kJ mol^{-1}

Solvent	T/°C	$K = N_g/N_t$	$\Delta G^{\circ a}$	$\Delta H^{\circ b}$	ΔE	$\Delta H^\circ - \Delta E$
(*a*) 1,1′-Dinitrobicyclopentyl						
CCl_4	5	6.293	−4.251	−3.925	−2.25	−1.675
	25	5.000	−3.988			
	45	3.719	−3.473			
Benzene	7	5.983	−4.165	−4.096	−5.81	1.714
	25	5.273	−4.119			
	45	4.504	−3.979			
(*b*) 1,1′-Dinitrobicyclohexyl						
CCl_4	5	0.652	0.989	0.796	2.59	−1.794
	25	0.720	0.812			
	45	0.811	0.555			
Benzene	25	3.256	−2.926	−2.921	−1.23	−1.691
	45	3.071	−2.966			
	60	2.808	−2.859			
(*c*) 1,1′-Dinitrobicycloheptyl						
CCl_4	5	0.152	4.354	4.200	5.99	−1.790
	25	0.188	4.140			
	45	0.214	4.074			
Benzene	7	0.495	1.637	1.590	3.32	−1.730
	25	0.517	1.636			
	45	0.568	1.495			

[a] ΔG° is calculated from the relationship $\Delta G^\circ = -RT\ln K$. [b] ΔH° is obtained from the slope of the ln K *versus* $1/T$ plot by the method of least-squares and assuming ΔH° to be constant over the temperature range studied.

bicyclohexyl. Unfortunately, MMP2 could not be used with the nitro compounds as the required parameters do not appear to be available.

As may be expected, the calculated barrier to internal rotation from the *gauche* to the *trans* form increases with ring size within each series. It is also significant that, in the solid state, the dinitro compounds exist in the *gauche* conformation whereas the dicyano compounds, based on our spectroscopic evidence, appear to prefer the *trans* conformation.

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