Rotational Isomerism in 3,4-Dimethyl-3,4-dinitrohexane

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I.r. and Raman spectra of 3,4-dimethyl-3,4-dinitrohexane (in the solid and solution states) are reported and assignment of frequencies made. It is assumed that the higher melting isomer has the *meso*- and the lower melting isomer the (±)-configuration. Comparison of the Raman and i.r. spectra of both the solid and solution states of *meso*-3,4-dimethyl-3,4-dinitrohexane shows that this compound exists in the *gauche* conformation in the solid state but as a mixture of *gauche* and *trans* rotamers in solution. 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 dielectric data shows that at 25 °C, *meso*-3,4-dimethyl-3,4-dinitrohexane exists as a rotameric mixture of 53% *gauche* and 47% *trans* in carbon tetrachloride solution, and 80% *gauche* and 20% *trans* in benzene solution. On the other hand, our spectral data suggest that in the solid state (±)-3,4-dimethyl-3,4-dinitrohexane exists as a mixture of the two possible rotamers in which the nitro groups are *gauche* to each other. In non-polar solvents like carbon tetrachloride, an additional rotamer, in which the nitro groups are *trans* to each other, appears. Analysis of the dipole moment data suggests that the combined proportion of the '*gauche*' rotamers is 24% in carbon tetrachloride and 43% in benzene.

Following our earlier studies on rotational isomerism in 2,3-dimethyl-2,3-dinitrobutane[1] and 2,2,3,3-tetranitrobutane,[2] we now report our findings on the related molecule 3,4-dimethyl-3,4-dinitrohexane based on dielectric, electric birefringence, i.r., and Raman spectroscopic measurements. Unlike the preceding two compounds, 3,4-dimethyl-3,4-dinitrohexane can exist in two diastereoisomeric forms, (±) and *meso*. Both diastereoisomers are capable of exhibiting rotational isomerism (Figures 1—3).

Experimental

Solute.—3,4-Dimethyl-3,4-dinitrohexane was prepared from 2-nitrobutane.[3] The two diastereoisomers were separated by passing the crude product through a silica gel column (60F-254) with 1:4 chloroform–hexane as eluant. The two isomers were further purified by recrystallization from absolute alcohol: *meso*-isomer, m.p. 88—89 °C (lit.,[3] 87—88 °C); (±)-isomer, m.p. 86—87 °C (lit.,[3] 85—86 °C). In accordance with general practice, it is assumed that this assignment is correct, *i.e.* the *meso* isomer has the higher m.p.

Solvents.—Solvents were carefully distilled and/or fractionated and dried before use. Their physical constants required in dielectric and Kerr effect measurements have been previously given.[4,5]

Apparatus.—Kerr constants were measured photometrically[6] while dielectric constants were determined with a heterodyne-beat meter.[7] Densities and refractive indices were measured by standard procedures.[8]

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. A Perkin-Elmer 682 i.r. 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 monochromator in conjunction with a photon-counting system set up in the Physics Department, National University of Singapore.

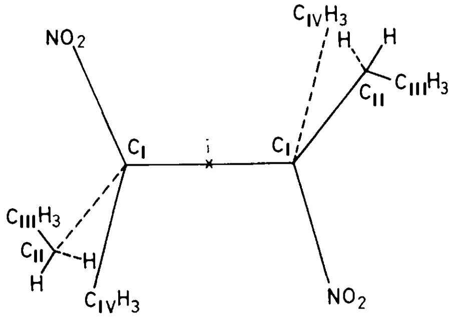
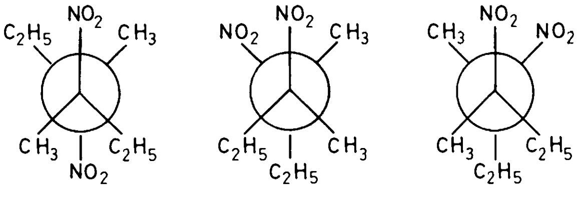
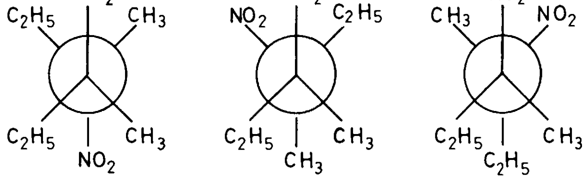


Figure 1.



(1) (2) (3)

Figure 2. Stable conformations of *meso*-3,4-dimethyl-3,4-dinitrohexane



(4) (5) (6)

Figure 3. Stable conformations of (±)-3,4-dimethyl-3,4-dinitrohexane

Results and Discussion

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

Table 1. (a) I.r. and Raman spectra of *meso*-3,4-dimethyl-3,4-dinitrohexane

Nujol	HB	KBr	CCl_4 ε_{20} = 2.238	CS_2 2.641	C_6H_6 2.284	$CHCl_3$ 4.806	CH_3CN 37.5	Raman solid	Raman CCl_4	Approximate group assignment
3 040(2)	3 040(3)	3 040(7)	—	—	×	×	×	—		νCH_3(as) νCH_2(as)
×	3 005(25)	3 015(59)	3 000(59)	2 995(46)	×	×	×	3 015(5)		
×	2 990(6)	2 995(9)	2 980(3)	2 980(16)	×	2 975(14)	×	2 986(24)		
—	—	—	—	—	—	—	×	2 977(6)		
×	2 960(9)	2 960(19)	2 950(11)	2 945(15)	2 950(57)	2 955(56)	×	2 954(17)		
×	2 895(9)	2 895(20)	2 890(25)	2 885(22)	2 880(18)	2 885(30)	×	—		νCH_3(sym)
×	2 870(½)	2 860sh(1)	2 845sh(1½)	2 850sh(1)	2 850sh(1½)	2 850sh(1½)	×	—		νCH_2(sym)
2 730(2)	2 760(1)	2 760(4)	2 755(2½)	2 755(1)	2 755(2½)	2 760(5)	2 760(3)	—		Combination
2 680(1)	2 680(½)	2 680(3)	2 675(6)	2 670(2½)	2 680(4)	2 680(7)	2 690(4½)	—		
2 390(1½)	2 390(3)	2 395(8)	2 395(4)	2 390(1½)	2 380(3½)	2 398(5)	2 390(4)	—		
1 585(1)	1 585(½)	1 586(3)	—	×	1 589(2)	1 590(2)	×	—		
1 565(2)	×	1 580(6)	—	×	1 568(5)	1 565(2½)	×	—		νNo_2(as)
1 547(43)	1 550(31)	1 555(53)	1 560(19)	×	1 550(74)	1 550(33)	×	1 555(11)		
1 540(4)	1 540(½)	1 544(9)	—	×	×	1 525(3)	×	1 540(7)		
1 507(2)	1 505(2)	1 510(4)	—	×	×	1 505(1)	×	1 523(2)		δCH_3(as) CH_2(bend)
—	1 470(15)	1 475(35)	—	×	×	1 475(1½)	×	—		
—	1 463(2)	1 468(2)	1 470(½)	×	×	1 460(1½)	×	1 467(2)	1 460(2)	
1 460br(62)	1 453(5)	1 457(9)	1 454br(30)	×	×	1 450(25)	×	1 454(2)	1 450(1)	
—	—	—	—	—	—	—	—	1 446(16)	—	
1 435(2)	1 433(5)	1 439(16)	1 435(8)	×	1 436(12)	1 435(2)	×	1 441sh(2)	1 435(7)	
1 400(12)	1 400(2)	1 399(3)	1 400(2)	×	—	1 400(1)	×	1 406(7)	1 400(8)	δCH_3(sym)
1 388(38)	1 392(14)	1 390(11)	1 392(28)	1 390(56)	1 395(22)	1 392(34)	×	—	—	
×	1 386(2½)	—	1 385(2½)	1 382(7)	1 382(13)	1 384(3)	×	1 390(1)	1 390(1)	
1 367(2)	1 365(2½)	1 371(7)	1 366sh(½)	—	1 368sh(1½)	—	×	1 370(3½)	1 370(1)	
1 351(10)	1 350(3)	1 353(9)	1 350(6)	1 350(3)	1 352(5)	1 345br(26)	×	1 355(14)	1 360(1)	νNO_2(sym)
1 339(9)	1 339(20)	1 341(46)	1 335(44)	1 338(73)	1 339(68)	—	×	1 345sh(6)	1 348(10)	
—	—	—	—	—	—	—	—	—	1 340(10)	
1 303(11)	1 302(12)	1 307(28)	1 305(15)	1 303(13)	1 306(18)	1 303(23)	×	1 310(4)	1 310(2)	CH_2(wag) and twist
1 294(9)	1 293(10)	1 297(23)	1 295sh(1½)	1 293sh(2)	1 298(3)	1 293(3)	1 293(17)	—	—	
1 190(2)	×	1 192(4½)	1 190(1½)	1 190(½)	×	1 185(½)	1 193(1½)	1 181(6)	—	ρCH_3 and $\nu C–C$
1 170(9)	×	1 175(27)	1 173(5)	1 173(4)	×	1 169(18)	1 176(12)	1 175(13)	1 173(5)	
1 146(14)	1 147(17)	1 149(22)	1 143(21)	1 144(15)	1 142(14)	1 143(24)	1 147(9)	—	—	
1 134(2)	1 135(2)	1 138(8)	1 135sh(½)	1 137sh(½)	1 136sh(1½)	1 136sh(½)	1 135(3½)	—	—	
1 120(15)	1 120(13)	1 122(54)	1 117(53)	1 118(46)	1 119(60)	1 118(66)	1 120(62)	—	1 105(2)	
1 056(8)	1 057(8)	1 059(16)	1 047sh(1)	1 047sh(1½)	×	1 051sh(½)	×	1 061(11)	—	CH_2(wag) and twist
1 048(13)	1 048(13)	1 050(36)	1 044(37)	1 043(21)	×	1 043(36)	×	1 054sh(2)	1 053(9)	
—	—	—	—	—	—	—	—	—	1 020(4)	
1 006(3)	×	1 010(8)	—	—	×	—	×	1 013(14)	1 011(8)	ρCH_3 and $\nu C–C$
997(14)	×	999(46)	998(25)	1 002(26)	×	1 002(57)	995(18)	1 001sh(2)	1 008(8)	
—	—	—	977(5)	979(4)	×	979(6)	980(1½)	—	—	
913(1½)	914(¼)	914(4)	—	—	—	909(1)	910(1½)	921(4½)	923(2)	
—	—	—	—	—	—	—	—	—	915(2)	
890(1)	×	890(1½)	888(1)	886(½)	887(1½)	886(4½)	890(3½)	—	—	$\nu C–N$
860(8)	×	862(13)	860(50)	858(30)	855(7)	860(13)	862(17)	867(19)	860(20)	
849(23)	×	852(55)	845(7)	845(9)	842(53)	845(52)	850(48)	—	—	
810(35)	×	813(67)	×	806(36)	808(40)	×	810(41)	813(8)	×	CH_2(rock)
—	—	—	×	800(5)	798sh(1½)	×	—	—	×	$\nu C–C$ and ρCH_3
×	759(9)	760(22)	×	757(12)	×	×	×	766(11)	×	
×	×	735(1½)	×	740(2)	×	×	×	737(5)	×	
680(2)	×	683(6)	×	685(1½)	×	×	683(2)	691(3½)	×	
663(½)	×	—	×	652(2)	×	652(5)	×	—	—	ρNO_2
640(6)	×	643(17)	638(9)	640(6)	×	635(15)	640(16)	647(4)	630(2)	
—	—	—	590(7)	590(2½)	×	590(6)	590sh(½)	—	—	$\delta C–C–C$
553(4)	555(8)	557(10)	552(1)	556(½)	555(2)	550(4)	550(3)	557(18)	570(10)	
519(18)	520(18)	521(50)	525(20)	525(9)	524(13)	520(32)	517(28)	521(31)	530(5)	
505sh(1)	505sh(1)	505sh(½)	513(3)	515(2)	516(4)	515(4)	510sh(½)	—	—	
—	—	—	486(4)	486(2)	488(2)	490(2½)	490(1)	—	—	

(b) I.r. and Raman spectra of (±)-3,4-dimethyl-3,4-dinitrohexane

×	3 039(3½)	3 045(8)	—	—	×	×	×	3 039(10)		νCH_3(as) νCH_2(as)
×	3 000(40)	3 010(64)	3 000(57)	3 000(53)	×	2 970(60)	×	2 991(7)		
×	2 990(2)	2 990(2)	2 979(9)	2 980(24)	×	2 960(1½)	×	2 973(43)		
×	2 960(7)	2 965(17)	2 955(4)	2 945(10)	2 955(57)	2 950(7)	×	2 957(11)		
×	2 920(1½)	2 935(1)	—	—	—	—	×	2 903(10)		
×	2 890(11)	2 900(20)	2 885(29)	2 885(29)	2 885(26)	2 885(32)	×	—		νCH_3(sym)
×	2 875(2)	2 880(4½)	2 850sh(2)	2 840sh(1)	2 820(1½)	2 845sh(1)	×	—		νCH_2(sym)
2 730(3)	2 770(1½)	2 760(4)	2 755(4)	2 760(2½)	2 755(3)	2 755(5)	2 760(4)	—		Combination
2 680(3½)	2 680(4)	2 680(6)	2 675(7)	2 670(3)	2 680(5)	2 680(8)	2 690(7)	—		
2 390(3)	2 398(3)	2 399(8)	2 390(4½)	2 395(2½)	2 380(3)	2 400(7)	2 385(8)	—		
1 551(50)	1 550(53)	1 545br(75)	1 555br(40)	×	×	1 550(68)	×	1 554(18)		νNO_2(as)

Table 1. (*continued*)

Nujol	HB	KBr	CCl_4 $\varepsilon_{20} = 2.238$	CS_2 2.641	C_6H_6 2.284	$CHCl_3$ 4.806	CH_3CN 37.5	Raman solid	Raman CCl_4	Approximate group assignment
1 505(1)	1 507(2)	1 510(6)	1 515(10)	×	×	1 505sh(1½)	×	1 535(1)		δCH_3(as) CH_2(bend)
1 477(½)	1 475(2)	1 476(7)	1 475sh(1)	×	×	1 475sh(1½)	×	1 475(1)		
1 475(½)	1 465(1½)	1 468(2½)	1 470(3)	×	×	1 470(2)	×	1 465(3)		
1 460(27)	1 455(16)	1 458(20)	1 460(28)	×	×	1 460(32)	×	—	1 460(2)	
1 452(1½)	—	1 451(2)	1 450(2)	×	×	1 448(2)	×	1 451(7)	1 450(1)	
—	1 433(5)	1 440(10)	1 435(1)	×	×	1 433(1½)	×	1 443(26)	1 400(3)	
1 400(3)	1 404(1)	1 405(3)	1 400(1)	×	1 392(19)	1 400(1½)	×	1 407(12)	1 400(4)	δCH_3(sym)
×	1 396(16)	1 399(32)	1 390(25)	1 388(66)	1 385(9)	1 390(34)	×	1 395(1)	—	
1 365(1)	1 365(1½)	1 371(3)	1 365(½)	1 365sh(½)	1 365sh(½)	1 385(1)	×	1 377sh(3)	—	
1 355(1)	1 355(1)	1 360(5)	—	—	—	—	×	1 353(2)	1 355(2)	
1 350(8)	1 348(22)	1 350(38)	1 348br(31)	1 348(74)	1 349(65)	1 340br(29)	×	1 349(26)	1 350(6)	νNO_2(sym)
1 340(½)	1 340(1)	1 344(4½)	1 339(½)	1 340sh(½)	1 340sh(1)	—	×	—	—	
—	—	—	1 328(5)	1 328(16)	1 330(7)	1 325(1½)	×	1 310(8)	—	CH_2(wag) and CH_2(twist)
1 308(8)	1 309(12)	1 310(22)	1 300(16)	1 300(16)	1 301(19)	1 299(15)	×	1 303(9)	—	
1 298(2½)	1 299(6)	1 300(10)	—	—	—	—	×	—	—	
1 227(1)	1 230(5)	1 230(5)	1 230(2)	1 230(½)	1 250(4)	×	1 230(2½)	1 227(4)	—	ρCH_3 and νC–C
—	—	—	—	—	—	—	—	1 195(3)	—	
1 190(½)	×	1 192(2)	1 173sh(½)	1 173sh(1)	1 190(3½)	×	1 190(1)	1 175(14)	1 187(2)	
1 170(11)	×	1 175(31)	1 160(11)	1 160(7)	×	×	1 171(17)	—	—	
1 143(7)	1 143(13)	1 146(23)	1 143(29)	1 143(19)	1 140(13)	1 142(24)	1 144(11)	—	—	
1 137(1)	1 137(1)	1 138sh(1)	—	—	1 130(1)	—	1 131sh(½)	1 135(2)	—	
1 121(21)	1 122(14)	1 126(63)	1 115(56)	1 116(46)	1 116(67)	1 116(64)	1 120(74)	—	—	
1 050(21)	1 050(26)	1 052(62)	1 049(46)	1 049(30)	×	1 045(31)	×	1 062(16)	1 050(5)	CH_2(wag) and CH_2(twist)
1 013sh(1½)	1 014sh(1)	1 015sh(2)	—	—	×	—	×	1 021(30)		ρCH_3 and νC–C
1 005(23)	1 005(4)	1 008(59)	997(33)	1 004(32)	×	1 005(55)	1 000(36)	—	1 005(3)	
992(3)	×	996(5)	980(1½)	980sh(1½)	×	983sh(1½)	980(6)	995(9)	—	
920(2½)	×	922(5)	925(2)	924(3)	928(2½)	—	920(1½)	925(2)	—	
890(½)	×	892(½)	—	—	892(½)	—	898(1½)	877(27)	—	νC–N
865(8)	×	868(39)	863(33)	862(19)	850(9)	864(32)	866(22)	—	860(12)	
847(21)	×	830(52)	840(45)	841(33)	840(47)	840(56)	850(45)	850(3)	—	
815(30)	×	819(75)	×	810(15)	812(26)	×	816(15)	822(24)	×	CH_2(rock)
805sh(1)	×	805sh(¼)	×	801(47)	800(32)	×	805(68)	—	×	νC–C and ρCH_3
×	761(7)	764(15)	×	—	×	×	750(4½)	766(16)	×	
730(9)	731(12)	735(24)	×	—	×	×	740(2)	740(10)	×	
680(2)	680(3)	682(6)	×	—	×	×	685(2½)	687(9)	×	
665(½)	×	665(1½)	×	664(12)	×	660(1½)	665(1)	—	—	ρNO_2
641(11)	×	646(26)	×	651(2)	×	637(15)	640(13)	649(8)	635(1)	
—	—	—	598(22)	598(9)	×	598(23)	595(7)	575(12)	580(8)	δC–C–C
549(4)	550(7)	551(8)	—	—	—	560(1)	560(2½)	554(20)	—	
523sh(1½)	521sh(2)	527sh(2)	—	—	—	—	535(½)	526(sh)	—	
510(20)	510(24)	515(50)	522(30)	523(13)	521(23)	521(31)	526(32)	514(39)	—	
492(5)	492(6)	497(9)	502(13)	503(9)	504(10)	504(12)	504(2)	501(9)		

The numbers in parentheses indicate relative intensities. × Indicates masking by background solvent or mulling agent. — Indicates absence of absorption. sh = Shoulder, br = broad. HB = Hexachlorobutadiene.

Spectroscopy.—(a) meso-3,4-*Dimethyl*-3,4-*dinitrohexane*. As this molecule is made up of 30 atoms, 84 fundamental modes are expected of it, given by $3N - 6$ where N is 30. This compound can exist as a mixture of the *trans* and two *gauche* rotamers which are mirror images of each other. Figure 1 shows the *trans* form. Here the two C_I–C_{II} bonds are taken to be non-freely rotating and the methyl groups $C_{III}H_3$ orientated as shown because of steric requirements.

The vibrational species of the 84 fundamentals of the *trans* and *gauche* rotamers are summarized in Table 3. The *gauche* rotamer, having no centre of symmetry, would have twice as many absorptions in the i.r. spectrum as the *trans*, as all the fundamental modes of the *gauche* rotamer are i.r. and Raman active while only half of these are active in either spectrum for the *trans*-rotamer.

meso-3,4-Dimethyl-3,4-dinitrohexane differs from 2,3-dimethyl-2,3-dinitrobutane[1] only in having two ethyl groups in place of two methyl groups. In making spectral assignments, we have taken advantage of our earlier study on the latter compound as well as the work of Sheppard[9] on n-paraffins. Comparing the spectra of *meso*-3,4-dimethyl-3,4-dinitrohexane with those of 2,3-dimethyl-2,3-dinitrobutane, we find extra bands at 813, 1 050 and 1 059 (doublet), 1 297 and 1 307 (doublet), and 2 860 cm^{-1} in the former. The band at 813 cm^{-1} with its characteristically strong intensity can be identified with the CH_2 rocking modes while the doublet at 1 297 and 1 307 cm^{-1} can be attributed to the CH_2 wagging and twisting vibrations. The band at 2 860 cm^{-1} is probably due to the symmetric CH_2 stretching vibration.

Inspection of the Raman and i.r. spectra in the solid state shows that the frequencies at which the bands occur are not mutally exclusive. Thus we conclude that the conformation in which the molecular rotamer exists in the solid state does not have any centre of symmetry. However, in the i.r. spectra in the solution states, a few extra bands at 486, 590, 800, and 979 cm^{-1} are observed and these bands are found to decrease in intensity with increasing polarity of the solvents. In fact, in the very polar acetonitrile solution, most of the bands, especially those at 590

Table 2. Polarizations, refractions, dipole moments, and molar Kerr constants at infinite dilution of 3,4-dimethyl-3,4-dinitrohexane and 2-nitrobutane

Temp. (°C)	Solvent	Conc. range ($10^5 w_2$)	$\alpha\varepsilon_1$	β	γ	δ	P_2/cm^3	R_D/cm^3	$10^{30}\mu^a$/Cm	$10^{27}\,{}_\infty({}_mK_2)$/ m^5 V^{-2} mol^{-1}
meso-3,4-Dimethyl-3,4-dinitrohexane										
6	Benzene	741—2 617	12.76	0.199			524.1		15.48 ± 0.05	
25	Benzene	755—5 062	11.10	0.258	−0.012	−24.58	478.0	48.7	15.25 ± 0.03	−499 ± 6
45	Benzene	740—2 601	9.42	0.245			430.0		14.79 ± 0.05	
5	CCl_4	462—1 261	13.18	−0.383			327.1		11.84 ± 0.10	
25	CCl_4	545—2 616	12.36	−0.368	−0.018	6.31	318.6	49.9	12.04 ± 0.07	5 ± 1
45	CCl_4	825—1 964	11.55	−0.352			311.7		12.24 ± 0.07	
25	Cyclohexane	647—1 453	6.06	0.352			340.3	49.8	12.51 ± 0.07	
(±)-3,4-Dimethyl-3,4-dinitrohexane										
25	Benzene	737—5 114	5.98	0.249	−0.017	−13.51	281.9	48.4	11.21 ± 0.03	−267 ± 6
25	CCl_4	682—2 366	5.49	−0.382	0.013	3.71	170.4	49.8	8.01 ± 0.03	6 ± 1
25	Cyclohexane	586—1 541	2.50	0.315			168.5	49.7	7.94 ± 0.07	
2-Nitrobutane					γ'					
25	Benzene	1 835—3 430	12.23	0.066	−0.119		270.0	27.0	11.48 ± 0.07	

[a] μ is calculated assuming that $_DP = 1.05\,R_D$.

Table 3.

Point group	Vibrational species	No. of fundamentals
C_i (*trans* rotamer)	A_g $3n - 3$	42
	A_u $3n + 3n_o - 3$	42
C_1 (*gauche* rotamer)	A $3n - 6$	84

and 800 cm^{-1}, are nearly not observable. These bands are thus assigned to the *trans* rotamer and their existence leads to the conclusion that only the *gauche* rotamer is present in the solid state. This is very similar to 2,3-dimethyl-2,3-dinitrobutane which has been found to exist only in the *gauche* form in the solid state and as a mixture of *gauche* and *trans* rotamers in solution. The very weak intensities of the bands attributed to the *trans* rotamer in acetonitrile shows the very small proportion of this rotamer 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.

Since the extra bands in solution are attributable to the *trans* rotamer, all the bands in the solid-state spectra must be due to the *gauche*. The doublet at 852 and 862 cm^{-1}, which can be assigned to the C–N stretching vibrations of the *gauche* form, is of particular interest. Diallo,[10] in his study of 2,3-dimethyl-2,3-dinitrobutane in the solid state, observed only two bands at 850 and 843 cm^{-1} attributable to the C–N vibrational modes. Since there should be one such active band for the *trans* rotamer (C_{2h}) state and two bands for the *gauche* rotamer (C_2), he concluded that 2,3-dimethyl-2,3-dinitrobutane exists in the *gauche* conformation in the solid state. In the case of *meso*-3,4-dimethyl-3,4-dinitrohexane, it is also expected that the *gauche* rotamer would have two C–N i.r. stretching bands while the *trans* should have only one. Thus, the presence of only the doublet supports our conclusion that only the *gauche* rotamer, and not the *trans*, exists in the solid state.

Comparison of the solid- and solution-state spectra shows that many bands decrease in intensity on dissolution, especially in non-polar solvents. Such bands are at 521, 557, 914, 1 059, 1 138, 1 175, and 1 297 cm^{-1} and are attributed to the *gauche* rotamer. The weak band at 914 cm^{-1} practically disappears in carbon disulphide and carbon tetrachloride but reappears in the very polar acetonitrile solution. Bands at 1 059, 1 138, and 1 297 cm^{-1} become very weak in carbon disulphide and carbon tetrachloride solutions in which they appear only as shoulders. The spectral features become very much like in the solid state in the very polar acetonitrile solution, showing that the *gauche* rotamer predominates in this solvent.

However, some bands are found to increase in intensity on dissolution in non-polar solvents. 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 their intensities. Two such bands are at 505 and 862 cm^{-1}. In the solid state the band at 505 cm^{-1} only appears as a shoulder to the stronger band at 521 cm^{-1}. However, on dissolution in carbon disulphide and carbon tetrachloride, the band at 521 cm^{-1} (due to the *gauche* rotamer) decreases in intensity so that the relative intensities are reversed. However, in solutions of benzene, chloroform, and acetonitrile, the relative intensities are reversed again. A similar situation occurs for the band at 862 cm^{-1}. In the solid state, it is of lower intensity than its neighbour at 852 cm^{-1}. However, in carbon disulphide and carbon tetrachloride, it has higher intensity than its neighbour and the situation is reversed in benzene, chloroform, and acetonitrile.

Bands at 590 and 486 cm^{-1} attributed to the *trans* rotamer of *meso*-3,4-dimethyl-3,4-dinitrohexane bear strong resemblance to the two bands at 598 and 495 cm^{-1} attributed to the *trans* rotamer of 2,3-dimethyl-2,3-dinitrobutane. These bands have been assigned to the symmetric C–C–C deformation modes.

Thus it can be concluded that *meso*-3,4-dimethyl-3,4-dinitrohexane exists in the *gauche* conformation in the solid state and as a mixture of *gauche* and *trans* rotamers in solution. In solvents like benzene, chloroform, and acetonitrile, the *trans* population is rather low.

(b) (±)-3,4-*Dimethyl*-3,4-*dinitrohexane*. The (+) and (−) isomers are spectroscopically equivalent. The stereochemistry of the carbon atoms involved is such that each enantiomer can exist as a mixture of three rotamers, all of which belong to C_2 symmetry.

Figure 3 gives the Newmann projections of the rotamers (**4**)—

(6) expected of the (+) or (−) form. Rotamer **(4)** has the C_2 symmetry axis as the only element of symmetry in the molecule. It would thus have 43 of the 84 fundamental modes associated with class A and 41 with class B. All the absorptions are expected to be both i.r. and Raman active as there is no centre of symmetry in the molecule. Although the rotamers **(5)** and **(6)** are not mirror-images of each other, each of them has the C_2 symmetry axis as the only element of symmetry and thus belongs to the C_2 point group.

Thus, all three rotamers of the (+)- or (−)-isomer are of the same point group. However, they are of different energies and some of their bands are not expected to coincide; thus it may be possible to identify the absorptions belonging to each of them.

Comparison of the solid-state i.r. spectra of the *meso* and the (±) isomers shows that they are very similar except for the extra band belonging to the (±)-isomer at 1 230 cm^{-1}. There are a few other very weak extra bands at 527, 805, and 1 015 cm^{-1} in the latter compound, but they appear as shoulders. Also, two bands at 497 and 735 cm^{-1} are of stronger intensity than their *meso* counterparts.

Inspection of the frequencies of the bands in the i.r. spectra of the (±)-isomer in the solid state shows that they are not mutually exclusive with those in the Raman spectra. This is as expected since all the rotamers of the (+) and (−) enantiomers have vibrational frequencies active in both types of spectra. Comparison of the solid- and solution-state i.r. spectra, however, shows that there are two extra bands in solution. These are found at 1 328 and 598 cm^{-1} and they decrease in intensity with increasing polarity of the solvents. Thus these extra bands must belong to a non-polar rotamer [rotamer **(4)** in Figure 3]. From the intensities of these bands in non-polar solvents like carbon disulphide and carbon tetrachloride, it can be concluded that there is a substantial proportion of this rotamer in these solvents. Thus it can be concluded that in the solid state, either one or two rotamers *e.g.* **(5)** and/or **(6)** with nitro groups *gauche* to each other are present while in solution, another rotamer **(4)** with zero dipole moment comes into existence.

Inspection of the i.r. solution-state spectra shows that some bands disappear in non-polar solvents like carbon disulphide and carbon tetrachloride. Such bands are found at 3 045, 2 935, 1 360, 1 300, 1 138, 1 015, 682, 551, and 527 cm^{-1}. However, some of them at 1 138, 682, 551, and 527 cm^{-1} are found to reappear in the very polar acetonitrile solution. These bands can be interpreted as belonging to a rotamer which is stabilized in the solid state through short-range crystal forces but become so destabilized in non-polar solvents as to disappear completely. However, in the very polar acetonitrile solution, probably due to stabilization by the 'reaction field' effect, it becomes stable enough to exist although, from the band intensities in acetonitrile solution, it can be concluded that even in this very polar solvent the proportion of the rotamer present is very small. Probably this rotamer has conformation **(5)** or **(6)**. Also these bands are found to be weak in intensity in the solid state, showing that the more stable of the two rotamers **(5)** and **(6)** is present in larger proportion than the other rotamer in the solid state. It is possible that the more stable rotamer is **(5)**, where the bulky ethyl groups are furthest apart. Thus it can be concluded that rotamers **(5)** and **(6)** are present in the solid state and this would explain the extra number of i.r. bands in the solid state of the (±) pair when compared with those of the *meso* compound which exists only in one conformation in the solid state.

Dipole Moment and Kerr Effect Measurements.—Results of the polarization measurements in benzene, carbon tetrachloride, and cyclohexane at various temperatures are summarized in Table 2. Kerr effect measurements in benzene and carbon tetrachloride are also included.

(a) meso-3,4-*Dimethyl*-3,4-*dinitrohexane*. Table 2 shows that the dipole moment of this compound increases with increasing temperature in carbon tetrachloride. This implies that ΔE, the internal energy difference between the rotational isomers (*i.e. gauche* and *trans*), is positive. Application of the Lennard Jones–Pike[11] method gives a ΔE value of 1.51 ± 0.4 kJ mol^{-1} with the dipole moment of the *gauche* rotamer (μ_g) equal to 16.51 × 10^{-30} Cm and its dihedral angle (2θ) equal to 80°. The corresponding proportion of the *gauche* rotamer in carbon tetrachloride solution is 53%. In calculating the dihedral angle (2θ) between the two C–C–NO_2 planes of the molecule $(CMeEtNO_2)_2$, we have used the equation $\mu(\theta) = 2\mu_0 \sin\alpha \cos\theta$, where μ_0 the moment of the symmetrical half of the molecule is equated to the moment of 2-nitrobutane; α, the supplement of the C–C–NO_2 bond angle is taken as 70°; and $\mu(\theta)$ the resultant moment of any conformation is equated to μ_g. Our spectroscopic results showing that, in non-polar solvents like carbon tetrachloride and cyclohexane, the *trans*-rotamer exists in appreciable concentration are broadly consistent with this value. The smaller ΔE value of *meso*-3,4-dimethyl-3,4-dinitrohexane (1.51 kJ mol^{-1}) compared with that of 2,3-dimethyl-2,3-dinitrobutane (2.52 kJ mol^{-1}) shows that replacement of two methyl groups by two ethyl groups has made the *gauche* rotamer of the dinitrohexane compound more stable than that of the dinitrobutane compound in carbon tetrachloride solution, probably because of greater steric repulsive interactions between the ethyl groups.

Like 2,3-dimethyl-2,3-dinitrobutane, the dipole moment of *meso*-3,4-dimethyl-3,4-dinitrohexane in benzene decreases with increasing temperature. This indicates that ΔE is negative and that, in benzene, the *gauche* rotamer is now more stable than the *trans*. Calculations show that ΔE has a value of −5.15 kJ mol^{-1} with μ_g 17.07 × 10^{-30} Cm and the dihedral angle 75°. The *gauche* rotamer population corresponding to these values is 80%.

There is also an augmentation of dipole moment in benzene relative to carbon tetrachloride (3.2 × 10^{-30} Cm) or cyclohexane (2.7 × 10^{-30} Cm). This solvent effect, which may be attributed to π-complex formation between benzene and the 'acidic' hydrogen atoms of the dinitro compound, is similar to the augmentation observed in the cases of 2,3-dimethyl-2,3-dinitrobutane[1] and 2,2,3,3-tetranitrobutane.[2] As in these compounds, the plot of solution dielectric constant against solute weight fraction shows curvature, again indicating the stabilization of the polar *gauche* rotamer by its own reaction field.[12] The $_mK$ value of *meso*-3,4-dimethyl-3,4-dinitrohexane in benzene (−499 × 10^{-27} m^5 V^{-2} mol^{-1}) is significantly different from that in carbon tetrachloride (5 × 10^{-27} m^5 V^{-2} mol^{-1}) thus providing independent confirmation of the solvent effect.

The thermodynamic quantities for the *trans*$\rightleftharpoons$*gauche* equilibrium for *meso*-3,4-dimethyl-3,4-dinitrohexane are very similar to those for 2,3-dimethyl-2,3-dinitrobutane (Table 4). In carbon tetrachloride in which no specific solute–solvent interaction is expected for both compounds, the difference between ΔH° and ΔE is positive, implying that the process of converting the *trans* into the *gauche* molecules is accompanied by an increase in volume, since the pressure remains constant. However, this increase is apparently smaller in the case of *meso*-3,4-dimethyl-3,4-dinitrohexane. On the other hand, in benzene solution, the difference between ΔH° and ΔE is negative for both compounds, implying a decrease in volume of the system when *trans* molecules are converted into the more stable *gauche*. This decrease in volume may be attributed to the more effective attraction between the *gauche* molecules and the solvent benzene molecules to form π-complexes, than the *trans*. The apparently greater decrease in volume in the case of *meso*-3,4-dimethyl-3,4-dinitrohexane suggests that a tighter solvent sheath is formed possibly due to the greater surface area of acidic hydrogen atoms available for π-complex formation.

Table 4. Thermodynamic quantities governing *gauche–trans* equilibrium in kJ mol^{-1} for *meso*-3,4-dimethyl-3,4-dinitrohexane

Solvent	Temp. (°C)	$K = N_g/N_t$	ΔG°	ΔH°	ΔE	$\Delta H^\circ - \Delta E$
CCl_4	5	1.06	−0.13			
	25	1.14	−0.32	2.1 ± 0.7	1.51 ± 0.4	0.59 ± 0.7
			(0.68)*	(3.8 ± 0.7)	(2.52 ± 0.05)	(1.3 ± 0.7)
	45	1.22	−0.53			
Benzene	6	4.63	−3.56			
	25	3.94	−3.40	−8.2 ± 0.6	−5.15 ± 0.4	−3.1 ± 0.6
			(−3.39)	(−2.7 ± 0.6)	(−1.67 ± 0.05)	(−1.0 ± 0.6)
	45	2.99	−2.90			

ΔG° is calculated from the relation $\Delta G^\circ = -RT\ln K$. 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. * Numbers in parentheses refer to corresponding values for 2,3-dimethyl-2,3-dinitrobutane.

(b) (±)-3,4-*Dimethyl*-3,4-*dinitrohexane*. The dipole moment of (±)-3,4-dimethyl-3,4-dinitrohexane in carbon tetrachloride and in benzene is lower than that of *meso*-3,4-dimethyl-3,4-dinitrohexane in the corresponding solvents by *ca.* 4×10^{-30} Cm. This contrasts sharply with most *meso*/(±) diastereoisomers where the dipole moment of the *meso* isomer is normally significantly lower (*e.g.* in stilbene dichloride[13]), but is analogous to the case of 2,3-dicyano-2,3-diphenylbutane[14] whose *meso* isomer also has a higher moment than the (±) diastereoisomer. It would appear that in (±)-3,4-dimethyl-3,4-dinitrohexane dipolar repulsions between the C–NO_2 dipoles must override steric interactions between the C_2H_5 groups so that rotamer (**4**) would be favoured. This has the effect of lowering the overall moment of the (±) isomer to such an extent that the moment of the *meso* isomer is now greater than that of the (±) isomer.

Assuming that the moments of rotamer (**5**) and (**6**) are equal and that their dihedral angles are equal to the values found for rotamers (**2**) or (**3**) in the solvents carbon tetrachloride and benzene, it is possible to calculate the combined proportion of the *gauche* rotamers (**5**) and (**6**). This turns out to be 24% in carbon tetrachloride and 43% in benzene. The corresponding figures for rotamers (**2**) and (**3**) of the *meso* compound are 53 and 80%, respectively. The proportions of (**5**) and (**6**) thus calculated are expected to be less reliable than those for (**2**) and (**3**) because rotamers (**5**) and (**6**) are not strictly equivalent to each other, and will differ in physical dimensions from (**2**) or (**3**); nevertheless, these calculated proportions accord well with conclusions derived from our earlier spectroscopic data, and should provide a fairly quantitative basis for discussion.

The dipole moment of the (±) compound in carbon tetrachloride (8.01×10^{-30} Cm) is not significantly different from that in cyclohexane (7.94×10^{-30} Cm) at 25 °C. However, that in benzene (11.21×10^{-30} Cm) is much higher than that in either carbon tetrachloride or cyclohexane. The augmentation of dipole moment in benzene relative to carbon tetrachloride is found to be 3.20×10^{-30} Cm, which is of equal magnitude to that of the *meso* analogue. This augmentation can again be explained partly by the 'reaction field' effect and partly by π-complex formation. This solvent effect is again confirmed by the very different ${}_{m}K$ values of the compound in the two solvents (-267×10^{-27} m^5 V^{-2} mol^{-1} for benzene and 6×10^{-27} m^5 V^{-2} mol^{-1} for carbon tetrachloride).

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