Rotational Isomerism in 1,2-Dinitro-1,2-diphenylethane and 2,3-Dinitro-2,3-diphenylbutane

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I.r. and Raman spectra of the *meso* and (±) isomers of 1,2-dinitro-1,2-diphenylethane and 2,3-dinitro-2,3-diphenylbutane are reported and assignment of frequencies made. Comparison of the Raman and i.r. spectra of both the solid and solution states of these four isomers provides information on the conformations they adopt in the various states. Thus, *meso*-1,2-dinitro-1,2-diphenylethane is shown to exist as a mixture of *gauche* and *trans* rotamers in the solid and solution states with the *trans* predominating in a series of solvents including benzene. There is evidence for the existence of the (±) isomer as three different rotamers in the solid but in only two different rotamers in solution. These are believed to be the non-polar and one of the polar rotamers. Similarly, *meso*-2,3-dinitro-2,3-diphenylbutane exists as a mixture of *gauche* and *trans* rotamers. However, the population of the *trans* rotamer here is considerably less than that of the *gauche* rotamer in the solid and possibly the solution state as well. The (±) isomer of 2,3-dinitro-2,3-diphenylbutane, like its ethane analogue, exists as three rotamers in the solid state and only two in solution. Dipole-moment (in C_6H_6, CCl_4, and C_6H_{12}) and Kerr-effect (C_6H_6 and CCl_4) measurements of these isomers are consistent with the spectral evidence.

Our recent studies on the rotational isomerism of symmetrically substituted nitroethanes have thus far involved alkyl groups.[1–3] To examine the influence of phenyl groups we have prepared and studied 1,2-dinitro-1,2-diphenylethane and 2,3-dinitro-2,3-diphenylbutane. As the two central carbon atoms in these two compounds are asymmetric, diastereoisomerism can be expected with each compound having *meso* and (±) isomers. Each of these four diastereoisomers may exist as one or more of the rotamers expected of such molecules.

Experimental

Solutes.—1,2-dinitro-1,2-diphenylethane was prepared from α-nitrotoluene which was obtained by the alkaline nitration of benzyl cyanide.[4] The isomers were purified from absolute alcohol,[5] *meso* isomer, m.p. 239–240 °C (lit.,[6] 234–236 °C); (±) isomer, m.p. 153–154 °C (lit.,[6] 154–155 °C). 2,3-Dinitro-2,3-diphenylbutane was prepared from α-nitroethylbenzene[7] which was dimerised using silver nitrate in dimethyl sulphoxide:[8] *meso* isomer, m.p. 148–149 °C (lit.,[8] 150 °C); (±) isomer, m.p. 140–141 °C (lit.,[8] 140–141 °C).

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.[9,10]

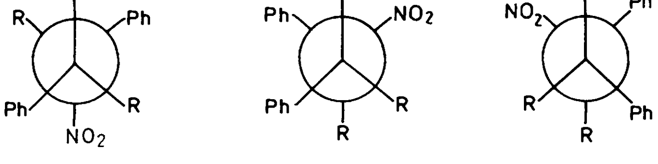
Apparatus.—Kerr constants were measured photometrically[11] while dielectric constants were determined with a heterodynebeat meter.[12] Densities and refractive indices were measured by standard procedures.[13]

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, University of Singapore.

Results and Discussion

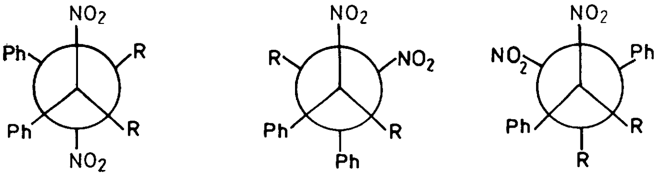
The results of physical measurements are presented in Tables 2 and 3 with standard notation. The low solubility of *meso*-1,2-dinitro-1,2-diphenylethane did not allow a good Raman spectrum of its solution to be recorded.

Spectroscopy.—(a) meso-*1,2-Dinitro-*1,2-*diphenylethane.* This molecule, comprising 32 atoms, can be expected to have 90 fundamental modes (Table 1). It can exist as a mixture of the *trans* and two *gauche* rotamers which are mirror images of each other, as shown in the Figure. As in 1,2-diphenylethane,[14] the



(1) *trans* **(2)** *gauche* **(3)** *gauche*

(±)isomer



(4) *trans* **(5)** *gauche* **(6)** *gauche*

Figure 1. Newman projections for the *trans* and *gauche* conformers of *meso*- and (±) (a) 1,2-dinitro-1,2-diphenylethane (R=H) and (b) 2,3-dinitro-2,3-diphenylbutane (R=CH_3). Isomer (**1**) is the *meso* form.

planes of the phenyl rings are assumed to be parallel to each other but not coplanar. From Leybold models, the rotation of the phenyl rings could be considered as hindered owing to the presence of the bulky nitro groups.

The spectra, listed in Table 2a, can be expected to be characterised by phenyl frequencies. Typically, these could be observed at 3 100–3 030 cm^{-1} for stretching modes, 2 000–1 970 cm^{-1} for the overtones and combination bands, and probably 1 250–1 000 and 931–720 cm^{-1} for the respective in-

Table 1.

Point group	Vibrational species	No. of fundamentals
C_i	A_g $3n - 3$	45
(*trans* rotamer)	A_u $3n + 3n - 3$	45
C_1		
(*gauche* rotamer)	A $3n - 6$	90

Table 2.

(a) I.r. (solid and solution states) and Raman (solid state) spectrum of *meso*-1,2-dinitro-1,2-diphenylethane

Nujol	HB	KBr	C_6H_6 0.40% Σ = 2.284 20	$CHCl_3$ 0.35% 4.806	CH_3CN 0.73% 37.5	Raman solid	Approximate group assignment
—	3 090(3)	3 100(2)	×	×	×	3 075(57)	
—	3 070(2)	3 080(6)	×	×	×	3 071sh(1)	νC–H (as)
3 030(4)	3 030(14)	3 040(23)	×	×	×	3 023(13)	
×	2 910(5)	2 910(10)	2 905(4)	2 915(6)	×		
—	2 800(1)	—	2 819(3)	—	×		νC–H (sym)
2 720(1)	2 720(1)	2 720(4)	—	2 715(1)	×		
—	1 999(27)	2 000(3)	—	—	—		Combinations/
—	1 975(2)	1 975(5)	1 976(3)	1 984(1)	—		overtones
—	×	1 627(4)	—	—	1 628(28)		
—	1 605(1)	1 605(2)	1 610(5)	1 605(15)	1 605(2)	1 605(57)	
1 590(3)	1 591(5)	1 592(9)	—	—	—	1 590(3)	νNO_2 (as)
1 567(2)	×	1 569(3)	1 575(2)	—	—	1 569(16)	
1 549(48)	1 549(66)	1 553(65)	1 565(61)	1 560(63)	1 571(41)		
1 544(1)	1 536(1)	1 542(8)	×	1 545sh(2)	×		νC–C
×	1 525sh(1)	1 525(2)	×	—	×		
1 500(5)	1 500(20)	1 500(22)	×	1 500(5)	×		
1 457(28)	1 467(21)	1 458(27)	×	1 459(13)	×	1 463(8)	
—	—	1 427(5)	×	1 420(3)	×		
1 395(1)	1 395(1)	1 397(5)	—	—	×		
1 378(8)	1 385(1)	1 389(3)	—	1 395(2)	×	1 365(45)	νNO_2 (sym)
1 360(26)	1 361(48)	1 362(56)	1 359(36)	1 355(49)	×	—	
1 339(6)	1 339(14)	1 340(21)	1 340(1)	1 338(3)	×	1 321(5)	
—	—	—	—	—	—	—	
1 300(3)	1 303(8)	1 305(15)	1 300(3)	1 300(3)	×	1 277(6)	
—	—	—	—	—	—	—	
1 250(10)	1 250(27)	1 251(43)	1 243(2)	×	1 253(20)	—	
1 230(4)	1 230(10)	1 231(17)	—	—	1 230(4)	1 205(52)	
—	—	—	—	—	—	1 195sh(2)	ρC–H
1 195(4)	1 196(6)	1 197(25)	×	×	1 196(12)	—	
1 178(2)	×	1 180(10)	×	×	1 187(2)	1 163(17)	
1 160(2)	1 162(1)	1 162(12)	×	×	—	—	
1 108(1)	1 109(2)	1 108(2)	×	×	1 105(3)	—	
1 077(6)	1 077(16)	1 078(32)	1 073(5)	1 075(9)	1 075(18)	1 031(33)	
1 030(5)	1 029(13)	1 030(25)	×	×	×	1 009(110)	
—	—	—	—	—	—	995(4)	
1 001(4)	1 000(8)	1 002(25)	×	1 002(6)	×	951(14)	
—	—	—	—	—	—	17(13)	
930(2)	×	931(10)	927(3)	920(3)	×	895(50)	
896(2)	×	898(13)	890(3)	894(5)	895(5)	—	νC–N
852(5)	×	853(28)	×	×	854(15)	810(23)	γC–H
—	—	—	—	—	—	—	
778(3)	×	779(15)	×	×	775(8)	717(13)	
725(33)	725(52)	726(63)	×	×	727(73)	699(4)	
692(15)	692(30)	694(40)	×	×	698(43)	—	
675(1)	×	676(1)	×	×	672(1)	—	
648(10)	×	650(35)	×	×	650(25)	622(26)	αCCC and
627(7)	628(15)	629(22)	×	×	628(8)	609(5)	φCCC
600(1)	600(3)	596(2)	—	600(2)	—		
521(8)	521(20)	523(38)	525(13)	525(18)	525(20)		
485(2)	485(3)	487(10)	485(2)	487(2)	—		
—	455(3)	472(2)	—	—	448(3)		
—	—	420(6)	—	415(3)	413(4)		

Table 2 (*continued*)

(b) I.r. and Raman spectrum of (+)-1,2-dinitro-1,2-diphenylethane in the solid and solution states

			CS_2	C_6H_6	$CHCl_3$	CH_3CN	Raman		
Nujol	HB	KBr	2.4% Σ = 2.641 20	5.0% 2.284	3.5% 4.806	4.2% 37.5	Solid	$CHCl_3$ 10%	Approximate group assignment
3 112(1)	3 115(1)	3 120(4)	3 110(5)	×	3 110(1)	×			
3 090(1)	3 090(1)	3 100(2)	3 100(10)	×	—	×	3 091(6)		
3 070(1)	3 075(1)	—	3 075(30)	×	3 090(2)	×	3 070(34)		νC–H (as)
3 045(1)	3 045(6)	3 050(6)	3 040(57)	×	3 060br(20)	×	—		
3 018(7)	3 020(23)	3 020(27)	3 010(14)	×	—	×	3 022(2)		
×	—	—	—	×	2 975(12)	×	3 001(14)		
×	2 915(8)	2 920(12)	2 915(22)	2 920(29)	2 915(37)	×			
2 730(2)	2 730(2)	—	2 710(8)	2 720(8)	2 720(9)	2 725(8)			
—	2 420(2)	—	2 430(2)	2 430(2)	2 430(1)	2 430(2)			νC–H (sym)
—	—	—	2 350(2)	2 350(4)	2 350(4)	2 350(4)			
1 992(2)	1 994(5)	1 996(5)	1 995(2)	1 995(1)	1 995(1)	1 995(4)			
1 970(2)	1 970(6)	1 973(8)	1 977(11)	1 975(6)	1 983(10)	1 978(9)			
—	—	—	1 955(21)	1 950(1)	1 961(21)	—			Combinations/ overtones
1 900(1)	1 900(3)	—	1 907(3)	1 912(2)	1 910(3)	1 910(6)			
1 885(1)	1 885(2)	—	1 890(10)	1 892(10)	1 890(13)	1 890(1)			
1 840(2)	1 840(1)	—	1 840(2)	1 842(1)	1 843(1)	1 840(1)			
1 823(2)	1 823(4)	—	1 829(4)	1 835(4)	1 830(1)	1 824(8)			
1 813(1)	1 813(3)	—	1 804(15)	—	1 810(16)	1 805(1)			
—	—	—	1 760(3)	1 765(3)	1 762(6)	1 783(5)			
—	—	—	—	—	—	—	1 606(40)	1 603(9)	
1 585(3)	1 585(2)	1 585(8)	×	×	—	1 586(58)	1 589sh(2)	1 588(4)	
1 567(8)	1 566(2)	1 569(8)	×	×	—	×	1 567(17)	1 562(5)	
1 556(53)	×	1 553(79)	×	1 565(68)	1 570br(57)	1 586(58)			
1 525(2)	—	1 525(6)	×	×	—	×	—		νNO$_2$ (as)
1 500(9)	1 500(18)	1 501(26)	×	×	1 498(15)	×	—	1 495(5)	
1 490(2)	1 490(2)	1 482(11)	×	×	—	×	—		
1 465(4)	1 473(1)	1 475(6)	×	×	—	×	—		
1 456(36)	1 458(31)	1 459(30)	×	×	1 455(30)	×	1 462(3)	1 455(4)	νC–C
1 420(1)	1 418(2)	—	×	×	1 425(1)	×	—		
×	1 394(3)	1 397(11)	×	×	1 385(2)	×	—	1 395(3)	
×	1 371(47)	1 376(64)	1 370(69)	1 370(69)	1 367br(54)	×	1 378(28)	1 370(9)	
×	1 359(1)	1 362(6)	1 355(5)	1 360(4)	1 350(2)	×	1 366(2)	1 350(5)	
×	1 330(1)	1 342(4)	1 340(1)	—	—	×	1 335(1)	1 335(4)	νNO$_2$ (sym)
1 320(1)	1 320(2)	1 322(1)	1 320(7)	1 326(3)	1 320(6)	×	—		
1 297(6)	1 298(13)	1 300(15)	1 296(26)	1 299(35)	1 296(28)	1 295(15)	—		
1 278(14)	1 279(26)	1 280(35)	1 273(32)	1 277(28)	1 273(22)	1 280(20)	1 286(2)	1 248(7)	
1 250(1)	1 250(2)	1 250(2)	1 240(4)	1 245(2)	×	1 250(2)	1 259(3)	1 230(8)	
1 190(6)	×	1 192(19)	1 188(25)	1 184(11)	×	1 190(25)	1 194(43)	1 187(19)	
1 185(3)	×	1 188(6)	—	—	—	—	—		
1 172(2)	×	1 175(4)	1 172(11)	×	1 170(31)	1 180(10)	1 179(2)		
1 160(4)	1 160(3)	1 162(10)	1 158(2)	1 157(11)	1 160(2)	—	1 165(16)	1 160(8)	βC–H
1 120(1)	1 120(2)	1 122(4)	1 114(1)	1 114(1)	—	—	—		
1 105(1)	1 107(2)	1 108(4)	1 103(10)	1 107(8)	1 105(10)	1 110(6)	—		
—	1 099(1)	1 099(3)	1 093(1)	1 100(1)	1 096(1)	1 100(3)	—		
1 073(8)	1 073(16)	1 076(22)	1 073(43)	1 075(42)	1 072(46)	×	—		
1 030(6)	1 030(13)	1 031(16)	1 030(42)	×	1 029(28)	×	1 034(42)	1 030(34)	
1 003(6)	1 003(8)	1 006(20)	1 001(25)	×	1 001(35)	×	1 009(105)	1 002(80)	
992(2)	—	996(4)	985(2)	989(9)	990(2)	×	989(2)		
975(3)	×	977(6)	—	—	—	×	—		
960(1)	×	964(2)	963(3)	965(3)	968(3)	×	—		
938(5)	×	940(15)	937(24)	940(30)	937(31)	940(20)	939(3)		
922(2)	922(3)	925(8)	—	—	—	×	—		
909(3)	909(4)	912(11)	915(8)	919(3)	917(1)	×	—		
900(4)	900(4)	903(5)	904(27)	908(22)	905(15)	×	907(56)	900(19)	νC–N
871(3)	872(2)	875(5)	870(2)	870(2)	870(5)	875(8)	881(7)	875(7)	
865(3)	×	867(10)	861(14)	861(19)	861(16)	866(18)	870(4)	865(8)	
846(2)	×	849(5)	837(7)	848(4)	×	×	851(5)	840(5)	γC–N
840(1)	—	841(2)	—	—	×	×	—		
800(4)	×	801(10)	793(24)	795(17)	×	800(18)	802(3)		
—	760(2)	760(2)	—	×	×	—	782(23)		
738(18)	748(15)	738(23)	740(3)	×	×	×	746(8)		
723(51)	724(46)	725(72)	720(82)	×	×	724(54)	—		

Table 2 (*continued*)

(b) I.r. and Raman spectrum of (+)-1,2-dinitro-1,2-diphenylethane in the solid and solution states

Nujol	HB	KBr	CS_2 2.4% Σ = 2.641 20	C_6H_6 5.0% 2.284	$CHCl_3$ 3.5% 4.806	CH_3CN 4.2% 37.5	Raman Solid	Raman $CHCl_3$ 10%	Approximate group assignment
697(sh)	700(sh)	702(sh)	—				707(4)		αCCC and φCCC
690(26)	690(33)	693(42)	689(33)	×	×	696(32)	697(2)		
673(4)	×	677(10)	673(3)	×	×	672(6)	678(9)		
628(18)	629(28)	630(36)	626(45)	×	620(20)	630(42)	635sh(2)	625(8)	
—	—	—	—		—	—	621(21)	615(11)	
603(10)	603(18)	606(27)	605(34)	601(18)	605(24)	608(29)	615(6)	605(8)	
583(14)	583(25)	586(28)	580(45)	580(35)	579(52)	580(35)	583(6)	575(6)	
531(15)	531(25)	533(36)	530(42)	530(38)	529(38)	530(28)	—	520(5)	
500(1)	499(2)	500(3)	500(3)	501(3)	500(2)	503(1)	499(12)	498(6)	
482(6)	482(13)	485(20)	483(27)	486(25)	482(27)	487(16)	485(5)	480(5)	
—	450(1)	450(2)	—	—	—	440(4)	—	455(4)	
—	—	430(4)	—	—	430(3)	435(3)	—		
417(2)	417(1)	423(5)	—	—	—	—	404(3)		

(c) I.r. and Raman spectrum of *meso*-2,3-dinitro-2,3-diphenylbutane in the solid and solution states

Nujol	HB	KBr	CCl_4 2.0% Σ = 2.238 20	CS_2 1.0% 2.641	C_6H_6 1.3% 2.284	$CHCl_3$ 2.7% 4.806	CH_3CN 3.1% 37.5	Raman Solid	Raman $CHCl_3$ 12.5%	Approximate group assignment
3 100(2)	3 104(2)	3 110(5)	3 100(15)	3 102(9)	×	3 095(5)	×	3 083(36)	3 081(37)	νC–H (as)
3 078(6)	3 080(6)	3 085(12)	3 068(25)	3 070(21)	×	—	×	3 079sh(2)	—	
3 045(4)	3 045(5)	3 050(10)	3 045sh(1)	—	×	3 050(17)	×	3 050(8)	—	
3 030(1)	3 030(1)	3 035(2)	3 030(21)	3 030(15)	×	3 000(2)	×	3 029(7)	×	
×	2 970(3)	2 975(6)	2 970(27)	2 970(15)	×	2 970(28)	×	2 970(20)	2 978(23)	
×	2 882(5)	2 884(8)	2 883(27)	2 890(13)	2 880(17)	2 885(28)	×		—	νC–H (sym)
2 680(2)	2 680(1)	2 680(3)	2 675(8)	2 675(4)	2 680(6)	2 680(8)	2 680(4)			
1 995(1)	1 995(1)	1 973(5)	1 978(6)	1 975(3)	1 970(5)	1 980(4)	1 980(7)			Combinations, overtones
1 970(2)	1 970(2)	—	1 960(14)	1 958(7)	1 960(1)	1 963(16)	—			
1 920(1)	1 920(1)	—	1 910(4)	1 910(2)	1 915(2)	1 910(4)	1 910br(5)			
1 895(2)	1 895(2)	1 895(2)	1 893(6)	1 890(3)	1 890br(9)	1 895(9)	—			
—	—	—	1 830(2)	1 830(2)	1 840br(7)	1 840(1)	1 825(7)			
1 813(4)	1 813(2)	1 815(7)	1 812(14)	1 808(7)	×	1 812(13)	1 810(1)			
1 765(2)	1 770(1)	1 765(7)	1 765(6)	1 760(3)	1 765(6)	1 765(6)	1 773(5)			
—	—	—	—	—	—	—	—	1 610sh(2)	—	νNO_2 (as)
1 603(2)	1 613(6)	1 604(8)	1 600(5)	×	1 600(5)	1 600(8)	×	1 603(25)	1 603(17)	
—	—	1 585(2)	—	—	1 585sh(4)	1 585(4)	×	1 587(12)	—	
1 568sh(2)	1 568(3)	1 569(5)	—	×	1 565(5)	—	×	1 555(12)	1 562(13)	
1 550(44)	1 550(38)	1 555br(52)	1 563(15)	×	1 550(45)	1 555br(30)	×	1 551(4)	1 558sh(3)	
1 538sh(1)	1 537sh(1)	1 543(6)	×	×	1 543sh(1)	—	×			
1 507(2)	1 507(3)	1 508sh(2)	1 504(39)	×	×	1 498(24)	×			
1 495(12)	1 495(7)	1 497(23)	1 490sh(2)	×	×	1 485(1)	×	—	—	
1 465(2)	1 480(1)	1 475(4)		×	×		×			νC–C
1 453(2)	1 453sh(1)	1 455sh(2)	1 460sh(4)	×	×	1 460sh(4)	×	1 457(8)	1 465(10)	
1 448(35)	1 445(21)	1 447(40)	1 447(42)	×	1 445(33)	1 447(45)	×	1 453(4)	—	
—	1 425(2)	1 425(5)	1 425sh(2)	×	—	1 415(2)	×			
×	1 390sh(1)	1 393sh(2)	1 388sh(1)	1 388sh(1)	1 393sh(3)	1 393sh(1)	×			
×	1 382(37)	1 385(50)	1 382(54)	1 380(56)	1 380(39)	1 383(39)	×	1 390(10)	1 395(8)	
1 348(30)	1 348(30)	1 348(49)	1 347(60)	1 343(63)	1 345(40)	1 348(46)	×	1 357(10)	1 354(10)	νNO_2 (sym)
1 340sh(1)	1 342sh(2)	1 343(4)	1 337(1)	—	1 339(1)	1 337(2)	×	1 349(4)	1 345(9)	
1 285(2)	1 285(1)	1 290(2)	—	1 285(1)	1 285(1)	×	1 285(8)			
1 275(1)	1 280(2)	1 295(1)	1 275(3)	1 275(2)	1 277(2)	×	1 278(3)	—	—	
—	—	—	—	—	—	×	—	1 226(16)	×	βC–H
—	—	—	—	—	—	—	—	1 222(4)	—	
1 205(20)	1 205(12)	1 207(30)	1 206(42)	1 207(32)	1 205(41)	×	1 208(43)	1 205(15)		
1 167(9)	1 165(16)	1 168(12)	1 161(6)	1 160(5)	1 152(8)	1 162(8)	×	1 170(16)	1 171(8)	
1 107(17)	1 108(13)	1 108(28)	1 103(50)	1 103(42)	1 103(43)	1 103(44)	1 100(38)	1 109(8)	1 109(8)	
1 078(10)	1 078(6)	1 080(17)	1 077(27)	1 078(20)	1 079(24)	1 078(25)	1 080(3)	—	—	
1 060(5)	1 060(3)	1 063(9)	1 061(37)	1 062(19)	1 061(10)	1 061(27)	×			
1 032sh(11)	1 032sh(2)	1 035(5)	1 031(50)	1 032(22)	×	1 030(29)	×	1 037(58)	1 038(66)	
1 028(15)	1 027(10)	1 030(26)	1 022(37)	1 023(7)	×	1 022(30)	×	—	—	
1 010(2)	1 010(1)	1 012(4)	—	1 008(2)	×	1 007(1)	×	1 007(90)	1 006(90)	
1 000(2)	×	1 005sh(1)	1 000sh(2)	1 002(2)	×	1 002(2)	×	—	—	

Table 2 (*continued*)

(c) I.r. and Raman spectrum of (+)-2,3-dinitro-2,3-diphenylbutane in the solid and solution states

			CCl$_4$ 2.0%	CS$_2$ 1.0%	C$_6$H$_6$ 1.3%	CHCl$_3$ 2.7%	CH$_3$CN 3.1%	Raman		Approximate group assignment
Nujol	HB	KBr	Σ = 2.238 20	2.641	2.284	4.806	37.5	Solid	CHCl$_3$ 12.5%	
990(1)	×	—	984(1)	985(2)	×	988(2)	990(4)			
971(4)	×	973(5)	968(3)	968(2)	968(10)	970(2)	975(3)			
928(4)	×	930(6)	920(30)	920(20)	921(24)	915(8)	928(5)			
880(2)	880(2)	884(2)	876sh(1)	878sh(2)	875(1)	875(1)	880(1)	885(16)	886(18)	
865sh(1)	×	870sh(1)	869(3)	870sh(2)	870sh(2)	870sh(2)	870sh(1)	866(12)	867(16)	νC–N
860(36)	×	862(52)	858(67)	856(52)	857(51)	860(60)	860(58)	862(4)	862sh	γC–H
849sh(2)	×	851(3)	846(3)	845sh(1)	845(2)	850sh(3)	850(4)			
787(34)	×	790(40)	×	785(49)	×	×	788(56)			
×	762(3)	768(5)	×	758(15)	×	×	×		×	
738(8)	738(8)	741(19)	×	738(16)	×	×	×	747(16)		
719(40)	719(30)	723(52)	×	718(45)	×	×	723(76)		—	
698(40)	698(30)	702(50)	697(63)	698(56)	×	×	702(73)	693(8)		
683sh(1)	682sh(2)	685sh(3)	675sh(1)	—	×	×	685sh(1)			
665(1)	×	—	663(2)	664(1)	×	×	665(2)		627(25)	αCCC
618sh(2)	620sh(3)	620sh(2)	617sh(1)	620sh(2)	×	615(1)	620sh(1)	623(31)	613(23)	and
604(36)	604(23)	607(39)	604(57)	607(39)	×	605(55)	605(44)	607(19)		φCCC
570(3)	570(2)	570(5)	565(8)	565(4)	565(6)	565(8)	565(5)			
509(15)	507(10)	512(20)	508(34)	509(20)	509(30)	509(32)	509(19)	509(5)	—	
478(6)	477(3)	480(12)	470(12)	470(8)	472(12)	472(13)	470(8)	—		
406(1)	406(1)	405(11)	406(2)	406(1)	407(3)	407(3)	406(2)	—		

(d) I.r. and Raman spectrum of *meso*-2,3-dinitro-2,3-diphenylbutane in the solid and solution states

			CCl$_4$ 3.0%	CS$_3$ 2.3%	C$_6$H$_6$ 3.8%	CHCl$_3$ 4.0%	CH$_3$CN 4.8%	Raman		Approximate group assignment
Nujol	HB	KBr	Σ = 2.238 20	2.641	2.284	4.806	37.5	Solid	CHCl$_3$ 28%	
—	—	—	3 170(3)	3 170(2)	×	3 170(2)	×			
3 105(2)	3 105(4)	3 110(4)	3 100(16)	3 100(15)	×	3 100(7)	×			
—	—	—	—	—	—	—	—	3 087sh(4)		νC–H (as)
3 080(4)	3 080(12)	3 080(14)	3 065(50)	3 065(54)	×	3 060(40)	×	3 082(52)		
×	3 050(8)	3 050(7)	3 045(3)	3 045(5)	×	—	×	3 049(4)		
×	3 035(3)	3 040(4)	3 030(28)	3 030(28)	×	—	×	3 041(13)		
×	3 010(10)	3 015(14)	—	3 015(1)	×	—	×	3 013(15)		
×	2 980(1)	—	—	—	×	2 995(2)	×	2 983(14)		
×	2 960(2)	2 965(2)	2 975(18)	2 970(15)	×	2 975(20)	×	2 963(6)		
×	2 940(1)	2 945(2)	2 940(1)	2 935(1)	×	2 940(2)	×	2 949(4)		
×	2 885(8)	2 885(12)	2 885(35)	2 885(25)	2 880(25)	2 890(38)	×			
2 730 (2)	—	2 690br(3)	2 710(1)	—	—	—	×			
2 680(2)	2 680(2)	—	2 670(8)	2 670(6)	2 675(5)	2 680(10)	2 680(5)			νC–H (sym)
—	—	—	2 415(4)	2 415(2)	2 410(2)	2 410(7)	2 395(3)			
2 360br(1)	—	—	2 360(2)	—	—	2 365(3)	×			
—	—	—	2 320(3)	—	—	2 325(5)	—			
1 985(2)	1 985(2)	—	1 956(14)	1 955(11)	1 975(6)	1 963(16)	1 975(8)			
—	—	—	1 903(9)	1 900(7)	1 900(7)	1 900(8)	1 910(5)			Combinations/
1 890(1)	1 890(3)	—	1 889(2)	1 888(2)	—	—	—			overtones
1 812(3)	1 811(5)	—	1 812(10)	1 805(10)	1 800(3)	1 812(13)	1 822(5)			
—	—	—	1 785(2)	—	1 781(3)	1 785(2)	1 785(4)			
—	1 770(1)	—	1 765(5)	1 765(4)	1 760(3)	1 765(5)	1 770(3)			
1 588(4)	1 589(3)	1 590(9)	1 601(4)	×	1 603(5)	1 603(5)	×	1 606(32)	1 600(4)	
1 565(3)	×	1 570(6)	1 573(1)	×	1 570(3)	1 585(2)	×	1 590(15)	1 585(2)	
1 546(65)	1 550(64)	1 555(71)	1 564(37)	×	1 555(58)	1 565(68)	×	1 561(4)	1 553(2)	
1 537sh(2)	1 536sh(1)	1 543(7)	—	×	1 538sh(2)	1 540(1)	×	1 549(10)	—	νNO$_2$ (sym)
1 525sh(1)	1 525sh(1)	1 525(4)	1 525(5)	×	×	×	×			
1 496(16)	1 497(22)	1 500(25)	1 498(54)	×	×	×	×	—	1 490(2)	
×	1 462(1)	1 456(1)	1 462(2)	×	×	1 463(4)	×	1 456(4)		νC–C
1 450(16)	1 449(49)	1 451(58)	1 446(41)	×	1 445(39)	1 449(62)	×	1 451(11)	1 445(2)	
1 423(1)	1 425(2)	1 428(5)	1 424(1)	×	—	—	×			
1 395(10)	1 394(37)	1 399(52)	1 391(39)	1 394(49)	1 390(1)	1 394(18)	×	1 397(6)	1 395(3)	
×	1 385(15)	1 389(18)	1 380(15)	1 380(24)	1 380(32)	1 382(46)	×	1 379(4)	1 380(6)	
1 350(44)	1 350(51)	1 353(57)	1 345(56)	1 350(74)	1 350(60)	1 350(44)	×	1 355(27)	1 350(6)	
1 341(1)	1 340sh(1)	1 346sh(3)	1 335(2)	1 340(3)	1 340(2)	1 335(3)	×			
1 328(3)	1 328(5)	1 332(3)	—	—	—	—	×	1 325sh(2)		
										νNO$_2$ (sym)

Table 2 (*continued*)

(d) I.r. and Raman spectrum of *meso*-2,3-dinitro-2,3-diphenylbutane in the solid and solution states

Nujol	HB	KBr	CCl_4 3.0% Σ = 2.238 20	CS_3 2.3% 2.641	C_6H_6 3.8% 2.284	$CHCl_3$ 4.0% 4.806	CH_3CN 4.8% 37.5	Raman		Approximate group assignment
								Solid	$CHCl_3$ 28%	
1 286(1)	1 286(2)	1 290(3)	1 283(2)	1 285(3)	1 285(2)	1 285(2)	1 285(2)			
1 229(8)	1 229(15)	1 231(20)	1 225(24)	1 228(19)	1 228(24)	×	1 230(31)	1 231(6)		βC–H
1 197(10)	1 198(6)	1 200(20)	1 197(38)	1 200(36)	1 196(15)	×	1 200(20)	1 202(55)	1 200(14)	
1 170(4)	×	1 170(4)	—	—	×	—	—	1 171(20)		
1 159(2)	×	1 162(5)	1 160(12)	1 162(13)	×	1 161(24)	1 162(8)	—	1 162(5)	
1 120(3)	1 120(4)	1 122(5)	1 117(5)	1 118(5)	1 120(3)	1 118(6)	1 120(4)	—	1 122(2)	
1 099(24)	1 100(34)	1 101(49)	1 094(56)	1 095(60)	1 096(41)	1 095(71)	1 095(41)	1 110(8)	1 100(4)	
1 073(14)	1 074(18)	1 077(22)	1 074(10)	1 075(9)	1 075(7)	1 074(9)	×	1 074(4)		
1 065(6)	1 067(10)	1 068(9)	1 062(6)	1 062(7)	×	1 061(8)	×		1 032(26)	
1 033(20)	1 035(24)	1 037(36)	1 032(60)	1 034(55)	×	1 030(40)	×	1 041(74)		
1 022(5)	1 024(6)	1 027(5)	—	—	×	—	×	1 025sh(2)	1 000(69)	
1 001(6)	1 001(3)	1 005(14)	1 000(3)	1 002(17)	×	1 002(27)	×	1 009(106)		
987(1)	×	990(2)	986(1)	987(2)	990(10)	989(2)	992(4)			
965(3)	×	969(5)	965(5)	966(4)	964(6)	969(5)	973(3)	970(4)	925(3)	νC–N γC–N
931(4)	×	934(8)	925(4)	924(4)	927(2)	925(1)	930(3)	935(4)	915(1)	
920(4)	920(2)	922(6)	918(24)	918(24)	920(18)	915(10)	908(7)	926(6)	895(6)	
896(3)	×	898(5)	890(7)	891(6)	892(6)	892(8)	895(4)	902(19)	878(5)	
—	—	—	—	—	—	—	—	885(4)	862(13)	
860(38)	×	864(60)	860(64)	860(67)	860(56)	861(69)	862(57)	866(19)	840(4)	
840(8)	×	842(16)	835(9)	839(20)	835(2)	838(9)	840(19)	849(8)	815(6)	
—	—	—	—	—	—	—	—	—		
782(30)	×	786(53)	×	780(57)	×	×	786(43)	793(4)		
×	768(2)	770(9)	×	770(7)	×	×	770(3)	775(20)		
737(15)	738(18)	740(26)	×	738(18)	×	×	740(5)	745(12)		
720(66)	720(54)	721(64)	×	720(77)	×	×	724(58)	729(3)		
708(3)	708(5)	710(5)	×	—	×	×	—	709(5)		αCCC and φCCC
697(41)	698(36)	699(28)	694(66)	696(34)	×	700(17)	690(4)	—	—	
665(1)	×	665(1)	664(1)	665(1)	×	×	665(1)	—	—	
626(6)	626(10)	629(10)	622(3)	626(6)	×	×	626(2)	633(15)	625(14)	
609(25)	610(30)	612(42)	612(35)	613(30)	602(18)	611(39)	614(31)	622(44)	618(14)	
546(6)	547(10)	547(13)	542(11)	544(9)	545(10)	543(12)	542(8)	549(4)		
519(11)	520(15)	520(24)	519(30)	520(27)	520(25)	520(33)	520(17)	521(6)	520(5)	
499(11)	499(15)	500(21)	493(15)	495(14)	497(12)	495(14)	494(6)	501(10)	490(4)	
470(5)	470(6)	471(8)	—	—	—	—	—	473(16)	465(1)	
428(1)	429(1)	435(2)	440(4)	440(2)	440(3)	438(5)	435(4)	—	435(3)	
417(1)	417(1)	419(10)	416(1)	—	416(1)	415(1)	417(1)	416(6)		

Numbers in parentheses indicate relative intensities. × Indicates masking by background solvent or mulling agent. — Indicates absence of band. HB = Hexachlorobutadiene.

plane and out-of-plane bending vibrations. The characteristic absorptions due to the five adjacent C–H in-phase out-of-plane wagging vibrations are found to be in the region 760–720 cm^{-1} for this compound.[15] The absorptions attributable to phenyl C–C stretching modes are expected in the region 1 627–1 395 cm^{-1}. The characteristic bands of these modes are observed at 1 592, 1 500, and 1 458 cm^{-1}. In-plane and out-of-plane ring and C–C–C deformations are probably responsible for absorption bands in the region 700–430 cm^{-1}.

The non-phenyl bands involve the methine and nitro groups. The absorption at 2 910 cm^{-1} is probably due to the methine asymmetric stretching vibration. The nitro asymmetric and symmetric stretching vibrations are likely to be found at 1 553 and 1 362 cm^{-1} respectively while the C–N stretching vibration is probably at 853 cm^{-1}.

Comparison of the i.r. and Raman spectra of the compound in the solid state shows that there are some bands (*e.g.* 1 321, 1 277, 1 205, 1 009, 951, and 810 cm^{-1}) present in the Raman spectra which are not present in the i.r. spectra. Furthermore there are some strong i.r. bands which are not observed in the Raman, *e.g.* 1 340, 1 251, 1 078, 779, 650, 523, and 487 cm^{-1}. Applying the mutual exclusion rule one could infer the presence of the *trans* form in the solid state and that these frequencies correspond to i.r. bands of the *trans* form. This conclusion is further strengthened by the observation that these frequencies tend to decrease in intensity relative to neighbouring frequencies in solution spectra using polar solvents like $CHCl_3$ or CH_3CN. Were they due to the *gauche* rotamer, their relative intensity would increase and not decrease in the polar environment of $CHCl_3$ or CH_3CN.

A few i.r. bands, *e.g.* those at 898, 853, and 726 cm^{-1} in the solid state, are found to increase in relative intensity in acetonitrile. The band at 726 cm^{-1} could be due to out-of-plane ring bending vibrations and/or in-phase out-of-plane C–H vibrations of the phenyl rings. As the *gauche* rotamer is expected to be stabilised in the polar acetonitrile solution, it can be concluded that these bands are due to the *gauche* rotamer. Thus there is a greater proportion of the *gauche* rotamer in acetonitrile than in the solid state.

Inspection of the spectra also reveals the presence of many coincident bands as well. This situation is similar to that of 2,2,3,3-tetranitrobutane[2] and it may be concluded that a mixture of *gauche* and *trans* rotamers exists in the solid and solution states. The low solubility of the compound even in

Table 3.

Polarisations, refraction, dipole moments, and molar Kerr constants at infinite dilution of 1,2-dinitro-1,2-diphenylethane and α-nitrotoluene. Incremental changes in the relative permittivities, densities, refractive indices, and Kerr constants (Δε, Δ*d*, Δn^2, and Δ*B*, respectively) were measured for solutions having solute weight fractions w_2. The coefficients α, β, γ, γ′, and δ were derived from the relations $\Delta\varepsilon_1 = \Sigma\Delta\varepsilon/\Sigma w_2$, $\beta d_1 = \Sigma\Delta d/\Sigma w_2$, $\gamma n_1 = \Sigma\Delta n/\Sigma w_2$, $\gamma' n_1{}^2 = \Sigma\Delta n^2/\Sigma w_2$ and $\delta B_1 = \Sigma\Delta B/\Sigma w_2 . a._{\infty}({}_{\mathrm{m}}K_2)$ refers to the solute molar Kerr constant at infinite dilution

Temperature (°C)	Solvent	Concentration range (10^5 w_2)	$\alpha\varepsilon_1$	β	γ	δ	P_2/cm^3	R_D/cm^3	10^{30} μ^a/C m	10^{27} ∞ (${}_{\mathrm{m}}K_{12}$)/ m^5 V^{-2} mol
meso-1,2-Dinitro-1,2-diphenylethane										
25	C_6H_6	200—284	1.74	0.358	0.048	19.82	148.4	69.8	6.41 ± 0.33	449 ± 12
(±)-1,2-Dinitro-1,2-diphenylethane										
25	C_6H_6	747—3 417	15.59	0.322	0.044	51.45	861.3	72.1	20.65 ± 0.10	1 026 ± 53
25	CCl_4	138—480	26.34	−0.106	0.150	345.79	815.1	71.8	20.05 ± 0.03	906 ± 11
25	C_6H_{12}	154—387	13.02	0.395			904.2	71.9	21.22 ± 0.23	
α-Nitrotoluene					γ′					
25	C_6H_6	4 188—11 339	9.37	0.259	0.041		276.4	36.5	11.38 ± 0.13	

Polarisations, refractions, dipole moments, and molar Kerr constants at infinite dilution of 2,3-dinitro-2,3-diphenylbutane and α-nitroethylbenzene

Temperature (°C)	Solvent	Concentration range (10^5 w_2)	$\alpha\varepsilon_1$	β	γ	δ	P_2/cm^3	R_D/cm^3	10^{30} μ^a/C m	10^{27} ∞ (${}_{\mathrm{m}}K_{12}$)/ m^5 V^{-2} mol
meso-2,3-Dinitro-2,3-diphenylbutane										
25	C_6H_6	635—2 185	13.91	0.330	0.050	49.92	854.4	80.3	20.45 ± 0.13	1 112 ± 14
5	CCl_4	265—652	27.43	−0.249			912.3		20.55 ± 0.03	
25	CCl_4	391—683	24.52	−0.214	0.131	466.22	847.1	81.3	20.35 ± 0.03	1 361 ± 18
45	CCl_4	579—738	21.73	−0.195			787.9		20.18 ± 0.07	
25	C_6H_{12}	274—625	11.04	0.392			854.9		20.45 ± 0.01	
(±)-2,3-Dinitro-2,3-diphenylbutane										
25	C_6H_6	709—2 634	10.71	0.316	0.050	23.05	674.7	81.5	17.88 ± 0.10	472 ± 4
25	CCl_4	115—230	18.29	−0.174	0.133	284.95	646.6	79.9	17.48 ± 0.20	829 ± 14
25	C_6H_{12}	199—488	7.88	0.423			624.6	80.3	17.15 ± 0.13	
α-Nitroethylbenzene					γ′					
25	C_6H_6	677—7 824	8.70	0.225	0.033		287.3	41.3	11.51 ± 0.07	
25	C_6H_{12}	939—4 812	7.22	0.302	0.086		296.5	41.0	11.74 ± 0.03	

[a] Calculated on the basis that ${}_{D}P = 1.05R_D$.

benzene and chloroform and the extensive masking by the solvents used, made it difficult to establish the relative distribution of the two rotamers in solution.

As may be seen in the Newman representations in the Figure, the *trans* rotamer is the most stable because non-bonded steric and dipolar repulsions are minimised in this conformation. The two *gauche* rotamers are less stable because, besides dipolar interactions, steric repulsions of the two bulky phenyl groups are present in these conformations.

(b) (±)-1,2-*Dinitro*-1,2-*diphenylethane*. The (+) and (−) isomers are spectroscopically equivalent. Each enantiomer can exist as a mixture of three rotamers, all of which belong to C_2 symmetry. Each would have 46 fundamentals associated with class A and 44 with class B, all 90 modes being both i.r. and Raman active. This implies that if all three rotamers of the (±)-form are present, the spectra would exhibit many more bands than the spectra of the *meso* form even if the latter consists of a mixture of *trans* and *gauche* rotamers. While the *gauche* rotamers with C_1 symmetry would have all their 90 modes active in both the i.r. and Raman spectra, the *trans* rotamers with C_2 symmetry would have only half of their 90 modes active only in the i.r. and the other half active only in the Raman. The Newman projections of the rotamers expected of the (±)-enantiomer are shown in the Figure [(**4**)–(**6**)].

The regions where the various phenyl, nitro, and methine vibrational modes are expected to occur should be similar to those of the *meso*-compound. As anticipated in the previous paragraph, comparison of the i.r. solid-state spectra of the *meso* and (±) isomers shows that there are many more bands in the spectra of the racemic mixture than those of the *meso* isomer.

Comparison of the Raman and i.r. spectra of the compound in the solid state [Table 2(b)] shows that coincidences of Raman and i.r. frequencies are evident here. This is as expected since all the rotamers of the racemic mixture belong to the C_2 point group where all the vibrational modes are i.r. and Raman active. Although it will be difficult to conclude from this whether one, two, or three rotamers are present in the solid state since all three rotamers belong to the same symmetry point group, an inspection of the i.r. spectra of the solution states leads us to conclude that at least two rotamers are present in the solid state. This is because some bands in the solid-state spectra are found to decrease in intensity while others increase in intensity on dissolution in solvents of varying dielectric constant, showing that they belong to different rotamers.

The i.r. bands which show a decrease in intensity with increasing dielectric constant of the solvent are most likely those associated with the non-polar rotamer (**4**) (Figure). An example of such a band is the one at 1 031 cm^{-1}. In the solid state it appears as a band of weaker intensity than its neighbour at 1 076 cm^{-1}. Its intensity increases in carbon disulphide but decreases in chloroform. Another example is the one at 1 322 cm^{-1}.

On the other hand, the bands which increase in intensity with increasing polarity of the solvent are in all probability those belonging to rotamers that are polar. Thus polar rotamers (**5**) and/or rotamers (**6**) could be present in the solid and solution states. Inspection of the i.r. spectra of the solution states also reveals additional lines in solution not observed in the solid state. These lines, *e.g.* 2 975, 2 350, and 1 961 cm^{-1} in the polar $CHCl_3$ solution spectra, could be the weaker bands of a polar rotamer like rotamer (**5**) or (**6**). Being polar, this rotamer would be stabilised in the polar $CHCl_3$ solution and be present in relatively high concentration thus enabling some of its weaker i.r. absorption lines to be clearly observed. The fact that these absorption lines are not observed in the solid-state spectra suggests that its concentration in this state is lower than the observable limit. The Raman spectra are consistent with this deduction. Raman lines in $CHCl_3$ solution, observed at 1 495, 1 395, 520, and 455 cm^{-1}, are not seen in the solid state. These frequencies could again be attributed to rotamer (**5**) or (**6**).

The relative intensities of the corresponding i.r. solid state and solution spectra are consistent with this view. An example is the i.r. band at 677 cm^{-1} in the solid state. It is found to decrease in intensity in non-polar solvents but increase in intensity in the more polar chloroform and acetonitrile solutions.

From the Figure, rotamer (**5**) may be considered to be the least stable because in this conformation, non-bonded steric repulsive and dipolar interactions are greatest. It is interesting to note that on dissolution in the various solvents, bands at 1 188, 977, 925, 841, and 423 cm^{-1} present in the i.r. solid state spectra disappear totally. These bands are, in all probability, due to rotamer (**5**). Stabilising short-range intermolecular interactions are likely factors which allow their existence in the solid state but not in solution where the molecules are too far apart for such interactions to take place. If our interpretation is correct, then all three rotamers (**4**)–(**6**) are present in the solid state while in solution, only the non-polar rotamer (**4**) and a polar rotamer [more likely (**6**)] exist, as rotamer (**5**) is, in all probability, too unstable to exist in solution.

(c) meso-2,3-*Dinitro*-2,3-*diphenylbutane*. This molecule differs from the previously discussed dinitrodiphenylethane in that the two hydrogen atoms bonded to the two central carbon atoms are now replaced by methyl groups. For this 38-atom molecule there would be 108 fundamentals. The *trans* rotamer would have 54 A_g and 54 A_u modes while the *gauche* would have all 108 as the A type. Except for these differences much of the discussion on the previous compound is relevant here.

Table 2(c) shows that this compound, like *meso*-1,2-dinitro-1,2-diphenylethane, has, but not to the same extent, a number of lines present in the Raman which are absent in the i.r. and *vice versa*. Examples of these are the Raman lines at 1 226 and 1 222 cm^{-1} and i.r. absorptions at 1 497, 1 080, and 1 030 cm^{-1}. The mutual exclusion rule suggests that these frequencies are associated with the *trans* rotamer.

Noting that the number of these mutually exclusive Raman and i.r. lines is smaller and less pronounced in *meso*-2,3-dinitro-2,3-diphenylbutane than in *meso*-1,2-dinitro-1,2-diphenylethane one could also conclude that the *trans* content of *meso*-2,3-dinitro-2,3-diphenylbutane is probably smaller than that of the ethane analogue.

On the other hand, there are many coincident bands as well. The solution spectra do not reveal any extra lines when compared with those in the solid state. Thus, we conclude that the butane analogue of *meso*-1,2-dinitro-1,2-diphenylethane exists as a mixture of rotamers in the solid and solution states. The presence of the *trans*-form in the solid state could be considerably smaller.

(d) (±)-2,3-*Dinitro*-2,3-*diphenylbutane*. As in the case of 1,2-dinitro-1,2-diphenylethane, solid-state spectra of the (±) isomer [Table 2(d)] have more lines than the *meso* rotamer. While the *trans* rotamer of the *meso* compound would have 54 A_g and 54 A_u modes with the *gauche* isomer having all 108 modes active in both i.r. and Raman, the (±) isomer here would have 108 modes made up of 55 A and 53 B types for each of its three different rotamers. These, though having different energies, have the same symmetry class, *i.e.* C_2. The Newman projections of these are shown in the Figure where $R = CH_3$.

The coincidence of Raman and i.r. frequencies can be easily seen in Table 2(d). This is consistent with the C_2 symmetry of the three rotamers mentioned earlier. An interesting phenomenon, observed in the case of (±)-1,2-dinitro-1,2-diphenylethane, is also noticed here. Solid-state i.r. bands at 1 332, 1 170, 1 027, 710, and 471 cm^{-1} do not seem to have corresponding absorptions in the i.r. solution spectra. This indicates the presence of rotamers, stabilised in the solid-state probably through short-range intermolecular forces in the close packing of the crystal lattice, which become destabilised in solution. Such rotamers could be (**5**) and/or (**6**), more likely (**5**). Here the nitro groups are *gauche* to each other. These *gauche* rotamers seem to be stabilised in the solid state for the dinitro ethanes studied so far.

In addition to the presence of a polar rotamer [which we suggest to be (**5**)] in the solid state, the existence of two other rotamers is suggested by spectral evidence. In the solution spectra some bands which also appear in the solid-state spectra increase in intensity with increasing polarity of the solvent. These appear to be associated with a polar rotamer like (**6**). The only other polar rotamer, (**5**), has been mentioned as the one which is stabilised in the solid state but not in solution. Table 2(d) also reveals the existence of i.r. solution bands at 2 415, 2 320, 1 903, and 1 785 cm^{-1}. These frequencies have no corresponding bands in the solid state. The relative intensities of these bands in the different solvents suggest that they belong to the polar rotamer (**6**). The fact that a few of the lines associated with rotamer (**6**) are not observed in the solid state shows that it may be present in the solid state in small quantities.

On the other hand, there are solution i.r. bands which decrease in intensity with increasing polarity of the solvent. This shows that a non-polar rotamer is present in both solid and solution. This rotamer is the non-polar (**4**). Hence the spectral evidence points to the presence of all three rotamers (**4**)–(**6**) in the solid state and only (**4**) and probably (**6**) in solution.

Dipole-moment and Kerr-effect Measurements.—Results of the polarisation and Kerr-effect measurements in various solvents and at specified temperatures are given in Table 3. The dipole moments of α-nitrotoluene and α-nitroethylbenzene, needed in the calculations for the dipole moments of the different conformations of these dinitro compounds, have been measured and are accordingly reported here.

(a) meso-1,2-*Dinitro*-1,2-*diphenylethane*. The dipole moment of this compound in benzene at 25 °C is 6.41×10^{-30} C m. This value is unusually low compared with those of most dinitroethanes. It also implies a high content of the non-polar *trans* rotamer (**1**). It has been postulated that the *gauche* rotamer of most dinitroethanes is stabilised as a result of the formation of π-complexes by the 'acidic' hydrogens of the solute with benzene. This increase in the *gauche* content induced by the solvent benzene is probably reduced in the present case as intramolecular interactions can take place between the 'acidic' hydrogen atoms and the π-electrons of the phenyl group in the compound instead of those in the benzene solvent molecules. The conditions for such intramolecular stabilisation are more favourable in the *trans* (**1**) than in the *gauche* conformation [(**2**) or (**3**)]. The *trans* conformation has two pairs of phenyl hydrogen groups where such interaction is maximised by the two groups being adjacent to each other, whereas the *gauche* rotamer has only one such pair. Hence we may expect the *trans* rotamer to be inherently more stable than the *gauche* rotamer. The dipole moment $\mu(\theta)$ of any conformer of a 1,2-disubstituted ethane $YR^1R^2C–CR^2R^1Y$ is given by equation (1)[16] where μ_0 is

$$\mu(\theta) = 2\mu_0 \sin \alpha \cos \theta \qquad (1)$$

the moment of the symmetrical half (CR^1R^2Y) of the molecules, α is the supplement of the C–C–Y bond angle, and 2θ is the dihedral angle between the two C–C–Y planes. Assuming α to be 70° and taking μ_0 to be equal to the dipole moment of α-nitrotoluene, *i.e.* 11.38×10^{-30} C m, $\mu(30°) = 18.52 \times 10^{-30}$ C m for a dihedral angle of 60°. This would correspond to a *gauche*:*trans* population ratio of 11:89. Deviations of ±10% in the values of α and the dihedral angle would result in the *gauche* population increasing to 14% or decreasing to 10.5%. The spectroscopic data are also consistent with a mixture of *gauche* and *trans* rotamers in the solid and solution states with the *trans* predominating even in benzene solution.

(b) (±)-1,2-*Dinitro*-1,2-*diphenylethane*. By contrast, the dipole moment of the (±)-diastereoisomer at 25 °C in benzene, carbon tetrachloride, and cyclohexane is 20.65, 20.05, and 21.22×10^{-30} C m, respectively. This large dipole moment suggests that the polar rotamers (**5**) and (**6**) with nitro groups *gauche* to each other are present in very high proportion in these three non-polar solvents.

The dipole moment of this isomer in benzene is comparable to its value in other non-polar and 'inert' solvents like carbon tetrachloride and cyclohexane. This suggests that complex formation between the compound and the benzene solvent molecules is much less important than in the case of other dinitro compounds.[1–3]

The essentially constant dipole moment indicates that intramolecular interactions here over-ride intermolecular interactions with solvent molecules although the existence of a small benzene solvent effect is suggested by the difference in ${}_{m}K$ values.[17–20]

The much larger dipole moment of the (±) rotamer relative to that of the *meso* isomer may be explained as follows.

In the *meso* isomer, the most favoured rotamer should be the *trans* (**1**) where both the polar nitro groups and the bulky phenyl groups are *anti* to each other. As this favoured rotamer has approximately zero dipole moment, the overall dipole moment of the *meso* form should be relatively low. By contrast, in the (±) isomer, the rotamer with zero dipole moment (**4**) has the bulky phenyl groups in the *gauche* position relative to each other. This less stable steric situation would thus cause the isomer to adopt the more favourable conformation labelled as (**5**) or (**6**). The appreciable dipole moment of rotamer (**5**) or (**6**) would thus cause the (±) isomer to have a larger dipole moment than the *meso* isomer.

Moreover, the favourable conformation of rotamer (**5**) or (**6**) is enhanced by intramolecular interaction between the hydrogen and phenyl groups as can be appreciated by examining Leybold models. These show that in rotamers (**5**) and (**6**), the 'acidic' hydrogen atoms are positioned in such a way that they can interact with the π-electrons above or below the planes of the phenyl rings. Such intramolecular hydrogen bonding is not possible for the non-polar rotamer (**4**).

(c) meso-2,3-*Dinitro*-2,3-*diphenylbutane*. The dipole moments of the *meso* compound in the three non-polar solvents of benzene, carbon tetrachloride, and cyclohexane at 25 °C (20.45×10^{-30}, 20.35×10^{-30}, and 20.45×10^{-30} C m, respectively) is very large and essentially constant. Assuming α to be 70°, and taking μ_0 to be equal to the dipole moment of α-nitroethylbenzene, 11.51×10^{-30} C m, application of equation (1) yields $\mu(20°)$ 20.3×10^{-30} and $\mu(40°)$ 16.56×10^{-30} C m for dihedral angles of 40° and 80°, respectively. Larger values of α, say 75°, would increase $\mu(20°)$ to 20.89×10^{-30} and $\mu(40°)$ to 17.03×10^{-30} C m. Thus, these calculations show that making allowances for deviations from normal values of α 70° and 2θ 60–70°, it appears likely that the *gauche* rotamer is present in a proportion close to 100%. This very high proportion suggests that rotamer (**2**), where the two NO_2 groups are *gauche* to each other, is much more stable than the non-polar rotamer (**1**) and is consistent with the fact that the methyl hydrogens being less 'acidic' than the hydrogens in 1,2-dinitro-1,2-diphenylethane, are less able to form complexes with phenyl groups. This also explains why the dipole moment of this *meso* compound is independent of solvent.

From the dependence of dipole moments on temperature, ΔE_s can be estimated.[21] The dipole moment in carbon tetrachloride was found to decrease with increasing temperature, showing again that the *gauche* rotamer is more stable than the *trans*. ΔE_s is calculated to be -3.71 ± 0.4 kJ mol^{-1} and the dipole moment of the *gauche* rotamer (μ_g) to be 21.45×10^{-30} C m in close agreement with some of the values estimated earlier.

The molar Kerr constant of the *meso* compound in benzene, ($1\,122 \pm 14 \times 10^{-27}$ m^5 V^{-2} mol^{-1}) is smaller than that in carbon tetrachloride ($1\,361 \pm 18 \times 10^{-27}$ m^5 V^{-2} mol^{-1}) indicating an apparently small solvent effect.[17–20] The molar Kerr constant value in benzene is probably the ${}_{m}K$ value of the complex formed between the *meso* compound and the solvent molecules rather than the 'true' value of the compound.

(d) (±)-2,3-*Dinitro*-2,3-*diphenylbutane*. The dipole moment of the (±) isomer in benzene, carbon tetrachloride, and cyclohexane at 25 °C is 17.88×10^{-30}, 17.48×10^{-30}, and 17.15×10^{-30} C m, respectively. The small variation of the dipole moment with change of solvent indicates that perhaps intramolecular interactions are more important than intermolecular interactions with solvent molecules. Also, the large values of the dipole moment show that the rotamers with nitro groups *gauche* to each other are present in greater proportion than the rotamer with nitro groups antiparallel to each other. This is supported by spectroscopic studies which show that in solution, rotamer (**6**) with nitro groups *gauche* to each other predominates.

The ${}_{m}K$ value in benzene (472×10^{-27} m^5 V^{-2} mol^{-1}) is lower than that in carbon tetrachloride (829×10^{-27} m^5 V^{-2} mol^{-1}) and this is probably due to complex formation between the (±) isomer and the benzene solvent molecules.[17–20]

In comparing the four compounds in this paper we note that while the dipole moment differences for the *meso* and (±) conformers of 1,2-dinitro-1,2-diphenylethane are as expected and explained, the differences for the 2,3-dinitro-2,3-diphenylbutane isomers are reversed. Next, hydrogen bonding between the hydrogen atoms and the phenyl rings within the latter molecule is minimal as the hydrogen atoms here are not as 'acidic' as in 1,2-dinitro-1,2-diphenylethane.

With these nitro compounds there is a tendency to exist in conformations with nitro groups *gauche* to each other in the solid state. There is also the tendency for the proportion of these conformers to be maintained as they go from the solid to the solution states. This is, in all probability, due to the rotation about the central C–C bond being hindered because of the phenyl rings being twisted out-of-plane. These steric factors force the molecules to adopt, in solution, the conformations they take in the solid state.

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Received 3rd *June* 1987; *Paper* 7/00050B