Rotational Isomerism in 2,3-Dinitro-2,3-dimethylbutane

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I.r. and Raman spectra of 2,3-dinitro-2,3-dimethylbutane (in the solid and solution states) are reported and assignments of frequencies made. Comparison of the Raman and i.r. spectra of the solid shows that the compound exists in the *gauche*-conformation in the solid state. Dipole moments in different solvents (benzene, carbon tetrachloride, dioxane, and cyclohexane) at different temperatures and molar Kerr constants (in carbon tetrachloride and benzene) are also reported. Analysis of the physical data shows that, at 25 °C, 2,3-dinitro-2,3-dimethylbutane exists as a rotameric mixture of 42% *gauche* and 58% *trans* in carbon tetrachloride solution, and 79% *gauche* and 21% *trans* in benzene solution. Solvent effects are also discussed.

Physical studies[1,2] on polar 1,2-disubstituted ethanes have shown that generally these compounds exist as mixtures of *trans*- and *gauche*-rotamers in the gaseous and liquid states, but only in the *trans*-conformation in the solid state. An exception to this pattern was observed for 1,2-dicyanoethane.[3] Above −43.7 °C, both *trans*- and *gauche*-rotamers were found to co-exist in the solid state, but below this temperature, only the *gauche*-rotamer is present. Le Fevre *et al.*[4] also showed that this compound exists in solution mainly as the *gauche*-rotamer where its concentration is three times that of the *trans*. The dihedral angle defining the *gauche*-conformation was also shown to have the unusually high value of 90°.

For the closely related molecule 2,3-dicyano-2,3-dimethylbutane, the normal pattern was found to apply.[5] The preferred rotamer in the solid state is the *trans* and in CCl_4 solution the equilibrium mixture comprises 82% of the *trans*- and 18% of the *gauche*-rotamer.[6] Our interest in these compounds has prompted us to study the dinitro-analogue, 2,3-dinitro-2,3-dimethylbutane, for comparison. This paper reports the results of a study on this compound, based on dielectric, electric birefringence, i.r., and Raman spectroscopic measurements.

Experimental

Solute.—2,3-Dinitro-2,3-dimethylbutane was prepared by a method described in the literature.[7,8]

Solvents.—All solvents were carefully distilled and/or fractionated and dried before use. The physical constants associated with their use in dielectric and Kerr effect measurements have been previously given.[6,9]

Apparatus.—Dielectric constants were determined with a heterodyne-beat meter[10] and densities and refractive indices by standard procedures.[11] Kerr constants were measured photometrically.[12]

The i.r. spectra of the solute in the solid state 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 monochromater in conjunction with a photon-counting system set up in the Physics Department.

Results

The results of all these physical measurements are presented in Tables 1—3 with standard notation.

Fundamental Vibrational Modes for the Rotational Isomers.—The *trans*-rotamer in this molecule of 24 atoms would have a total of 66 fundamentals as given by ($3N - 6$) where N is the number of atoms. It belongs to the C_{2h} point group. The symmetry properties of this conformation can then be used to deduce the number of fundamentals belonging to the various vibrational types and their activity in the i.r. and Raman spectra.

The vibrational species of the 66 fundamentals are designated according to the symmetry operations which they represent:

	Vibrational species	No. of fundamentals	Skeletals	Methyl
A_g	$3n + 2n_h - 1$	18	9	9
A_u	$3n + n_h + n + n_0 - 1$	16	7	9
B_g	$3n + n_h + 2n - 2$	15	6	9
B_u	$3n + 2n_h + 2n + 2n_0 - 2$	17	8	9
	Total	66	30	36

The A_u and B_u types are i.r.-active while A_g and B_g give rise to Raman lines. Since the C_{2h} point group possesses a centre of symmetry, the rule of mutual exclusion would hold for this conformer. The fundamental modes of the *trans*-rotamer are listed in Table 2. Here such notations like ν for stretching, δ for bending, ρ for rocking, and τ for torsional modes and the abbreviations sym for symmetric and as for asymmetric are used. Thirty-six of the vibrations involve the methyl group. The *gauche*-rotamer has only a C_2 axis of symmetry and thus belongs to the C_2 point group. Accordingly, it would have 34 *A*-type fundamentals (16 skeletals and 18 methyls) and 32 *B*-type ones (14 skeletals and 18 methyls). All the vibrations are both i.r. and Raman-active.

Discussion

The *trans*-rotamer of this compound would have 33 i.r.-active fundamentals due to the A_u and B_u modes. A large number of these frequencies should occur within the spectral region 4 000—400 cm^{-1}. Thirty-three other fundamentals due to the A_g and B_g modes would be Raman-active. The *gauche*-isomer

Table 1. I.r. and Raman spectra of 2,3-dinitro-2,3,-dimethylbutane in the solid and solution states

Nujol	HB	KBr	CCl_4 (1.2%) ε_{20} 2.238	CS_2 (0.8%) 2.641	C_6H_6 (5.6%) 2.284	$CHCl_3$ (2.3%) 4.806	CH_3CN (6.0%) 37.5	Raman solid	Raman $CHCl_3$ (4.1%)	Approximate group assignment
3 035 (4)	3 035 (22)	3 040 (17)	3 020sh (3)	3 020 (5)	X	X	X	3 037 (22)	X	νCH_3 (as)
X	3 010 (19)	3 020 (17)	3 005 (41)	3 000 (35)	X	2 998 (42)	X	3 011 (24)	X	
X	2 970 (14)	2 970 (10)	2 960 (34)	2 960 (17.5)	2 958 (55)	2 960 (48)	X	2 971 (26)	2 970 (31)	
—	—	—	—	—	—	—	—	2 965 (5)	2 965 (19.5)	
—	—	—	—	—	—	—	—	2 942 (4)	2 953 (11)	
X	2 875 (24)	2 880 (23)	2 882 (32)	2 880 (16.5)	2 882 (59)	2 882 (40)	2 860 (10)	2 921 (3.5)	—	νCH_3 (sym)
2 685 (2.5)	2 680 (6)	2 680 (5)	2 680 (7)	2 680 (4)	2 680 (17)	2 680 (12)	2 680 (14)	—	—	2 × δCH_3 (sym)
2 390 (1)	2 390 (4)	2 390 (4)	2 395 (4)	2 395 (2)	2 395 (12)	2 400 (7)	2 390 (11)	—	—	
—	—	1 568 (4.5)	—	—	—	—	—	—	—	
1 552 (72)	1 555br (62)	1 553 (55)	1 562 (35)	X	1 565br (75)	1 555br (66.5)	X	1 546 (19)	—	νNO_2 (as)
1 540sh (4)	1 540 (2)	1 540 (9)	1 545 (2)	X	—	—	X	1 534 (9)	1 519 (17)	
1 525 (2)	1 525 (1.5)	1 525 (9)	1 530 (6)	X	X	—	X	—	—	
X	1 471sh (3)	1 473 (8)	1 473sh (1)	X	X	—	X	1 489 (10.5)	1 503 (10)	δCH_3 (as)
1 460 (56)	1 455 (31)	1 456 (39.5)	1 460 (60)	X	X	1 460br (53)	X	1 465 (12)	—	
X	1 437 (11)	1 439 (15)	1 438sh (1)	X	X	—	X	1 441 (15)	—	
1 411 (18)	1 412 (33)	1 413 (52)	1 410 (17)	X	1 410 (22)	1 410 (34.5)	X	1 415 (13.5)	—	δCH_3 (sym)
1 397 (16)	1 396 (11)	1 398 (30)	1 394 (24)	1 395 (36)	1 400 (2.5)	1 393 (17)	X	1 403 (4.5)	—	
X	1 381 (35)	1 384 (41)	1 381 (54)	1 380 (67)	1 380 (26)	1 380 (23)	X	1 383 (4.5)	—	
—	1 347 (0.5)	1 348 (4.5)	1 345 (1)	—	1 348 (3)	1 345 (2)	X	1 345 (33)	1 354 (20)	νNO_2 (sym)
1 344 (34)	1 344 (42)	1 343 (59)	1 341 (50)	1 342 (66)	1 338 (46)	1 340 (45)	X	—	—	
1 240 (1.5)	1 241 (6)	1 240 (7.5)	—	1 245 (1.5)	1 253 (4)	1 247 (4)	1 240 (3)	1 244 (9)	1 235 (12)	ρCH_3 and νC–C
1 220 (3)	1 220 (14.5)	1 222 (21)	1 223 (5)	1 220 (2)	1 220 (9)	X	1 220 (15)	1 218 (8)	X	
1 172 (23)	X	1 174 (60)	1 172 (47)	1 171 (51)	1 155 (11)	1 170 (59)	1 173 (73)	1 030 (7)	1 022 (8)	
—	—	1 440sh (1)	—	1 135sh (3)	1 149 (3)	—	—	—	—	
1 134 (28)	1 136 (43)	1 136 (70)	1 128 (55)	1 128 (44)	1 129 (76)	1 135br (50)	1 136 (60)	—	—	
1 016 (2.5)	1 017 (4)	1 017 (6)	1 005br (4)	1 010 (2.5)	X	1 010 (6)	X	—	—	
—	X	950 (2.5)	948 (6)	948 (5)	948 (19)	947 (17)	949 (19)	955 (6.5)	—	
—	X	940 (2.5)	—	—	—	—	—	943 (10.5)	938br (23)	
—	X	930 (2.5)	—	—	923 (0.5)	925sh (3)	925sh (6)	931 (5)	—	
—	X	—	890 (6)	889 (3.5)	889 (10)	889 (8)	890sh (3)	—	—	
855sh (3)	X	857sh (2)	—	—	854 (6)	850br (57)	857 (1.5)	861 (45)	862 (28.5)	νCN
850 (33)	X	853 (71)	850 (59)	849 (54)	848 (74)	—	851 (75)	—	826 (21.5)	
—	—	—	—	—	843sh (4)	—	—	—	—	
766 (4.5)	768 (14)	768 (17)	X	765 (7.5)	760 (21)	755 (6)	760 (24)	769 (42.5)	X	νC–C and ρCH_3
X	735 (7)	735 (9.5)	X	738 (7.5)	733 (10)	730 (8)	735 (9)	741 (7.5)	745 (9)	
680 (1)	X	683 (7)	675 (3)	675 (1)	X	X	686 (7.5)	687 (6)	X	
646 (4)	—	648 (16)	644 (5.5)	643 (5.5)	X	643 (15)	645 (27.5)	650 (4.75)	661 (14)	ρNO_2 (sym)
—	—	—	598 (11)	598 (7)	597 (11)	598 (11)	595sh (6)	—	—	δC–C–C
565 (1)	567 (4)	570 (5.5)	570sh (1)	570sh (1)	569 (7.5)	568 (6)	568 (15)	563 (25)	571 (15)	
523 (10)	524 (29)	525 (34)	535 (12)	533 (9)	532 (27.5)	532 (24)	521 (28)	523 (39.5)	—	
510 (3)	512 (4)	513 (6.5)	—	—	—	—	511 (4)	514sh (7.25)	—	
—	—	—	492sh (3)	495sh (2.5)	500 (13)	500 (5)	493sh (1)	—	—	
—	430 (4)	435 (5)	440 (5)	437 (3)	437 (12)	435 (8.5)	437 (6)	—	—	

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

Table 2. Fundamental modes for *trans*-conformer of 2,3-dinitro-2,3-dimethylbutane

Fundamental mode	A_g	B_g	A_u	B_u
νCH_3 (as)	2	2	2	2
νCH_3 (sym)	1	1	1	1
δCH_3 (as)	2	2	2	2
δCH_3 (sym)	1	1	1	1
ρCH_3	2	2	2	2
τCH_3	1	1	1	1
νCC_2 (as)		1	1	
νCC_2 (sym)	1			1
δCC_2 (bend)	1			1
ρCC_2		1	1	
ρCC_2 (wag)	1			1
ρCC_2 (twist)		1	1	
νNO_2 (as)		1	1	
νNO_2 (sym)	1			1
δNO_2 (scissors deformation)	1			1
ρNO_2	1			1
ρNO_2 (wag)		1	1	
νCN	1			1
$\delta C\text{–}C\text{–}NO_2$ (sym)	1			1
$\delta C\text{–}C\text{–}NO_2$ (as)	1		1	
τNO_2		1	1	

Table 3. Molar polarisations, refractions, dipole moments, and molar Kerr constants at infinite dilution of 2,3-dinitro-2,3-dimethylbutane and 2-nitropropane

Incremental changes in the relative permittivities, densities, refractive indices, and Kerr constants ($\Delta\varepsilon$, Δd, Δn, Δn^2, and ΔB, respectively) were measured for solutions having solute weight fractions w_2. The coefficients α, β, γ, γ', and δ were derived from the relations $\alpha\varepsilon_1 = \Sigma\Delta\varepsilon/\Sigma w_2$, $\beta d_1 = \Sigma\Delta d/\Sigma w_2, \gamma n_1 = \Sigma\Delta n/\Sigma w_2, \gamma' n_1{}^2 = \Sigma\Delta n^2/\Sigma w_2$, and $\delta B_1 = \Sigma\Delta B/\Sigma w_2$. When the plots of $\Delta\varepsilon$ *versus* w_2 showed curvature, as in the case of benzene and dioxane solutions, 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 determined. α Was then derived from $\alpha\varepsilon_1 = a$. $_\infty(_mK_2)$ Refers to the solute molar Kerr constant at infinite dilution

Temperature (°C)	Solvent	Conc. range ($10^5 w_2$)	$\alpha\varepsilon_1$	β	γ	γ'	δ	P_2/ cm^3	R_D/ cm^3	$10^{30}\mu^a$/ C m	$10^{27}\ _\infty(_mK_2)$/ m^5 V^{-2} mol^{-1}
2,3-Dinitro-2,3-dimethylbutane											
25	Benzene	724—3 159	9.76	0.280	−0.012	−0.033	−0.70	366.7	40.0^b	13.28 ± 0.03	−68
45	Benzene	941—3 526	8.70	0.292				343.8		13.18 ± 0.03	
60	Benzene	994—3 593	7.85	0.295				323.2		13.08 ± 0.03	
5	CCl_4	440—577	10.22	−0.328				226.8		9.67 ± 0.10	
25	CCl_4	349—472	10.01	−0.266	0.027	0.057	48.84	227.8	40.8	10.04 ± 0.10	79
45	CCl_4	541—611	9.43	−0.320				226.5		10.31 ± 0.10	
25	Cyclohexane	98—166	4.37	0.364		0.061		221.5	42.2	9.81 ± 0.30	
25	Dioxane	691—4 818	12.43	0.144		0.053		401.1	40.5	13.94 ± 0.07	
2-Nitropropane											
25	CCl_4	2 132—5 055	26.49	−0.595		−0.148		276.1	21.3^c	11.74 ± 0.07	
25	Benzene	3 010—9 476	14.51	0.102		−0.148		269.9	20.8	11.61 ± 0.07	

[a] Calculated on the basis that $_DP = 1.05\ R_D$. [b] R_D(calc.) = 41.3 cm^3. [c] R_D(calc.) = 21.7 cm^3.

would have approximately twice as many i.r. bands as the *trans* since all the fundamentals are active in both the i.r. and Raman spectra. However, the internal vibrations of the CH_3 groups would prevent a certain number of bands from being observed in both rotamers, because of considerable overlapping and masking.

In making group vibrational assignments as shown in Table 1, we have made correlations with the vibrational frequencies of the bromo,[13] chloro,[14] cyano,[5] and phenyl[15] analogues of this compound and the useful assignments based on the normal co-ordinate calculations of 2,2,3,3-tetramethylbutane.[16] These compounds resemble 2,3-dinitro-2,3-dimethylbutane in that two bromo, chloro, cyano, phenyl, or methyl groups respectively replace the two nitro groups in our compound.

The vibrational modes and observed frequencies may be discussed as follows.

(i) CH_3 *Stretching and Deformation Frequencies.*—The number of modes associated with these frequencies, together with the region with which they are associated, are: CH_3 asymmetric stretching (4R, 4 i.r.) 3 040—2 940 cm^{-1}, CH_3 asymmetric stretching (2R, 2 i.r.) 2 930—2 860 cm^{-1}, CH_3 bending (4R, 4 i.r.) 1 490—1 440 cm^{-1}, and CH_3 symmetric deformation (2R, 2 i.r.) 1 415—1 370 cm^{-1}. The frequencies of the in-phase and out-of-phase vibrations of the individual CH_3 groups associated with most of the above modes are coincident, resulting in fewer bands than the expected number being observed. The assignment is quite straightforward, as is shown in Table 1.

(ii) C–C *Stretching and* CH_3 *Rocking Vibrations.*—The bands associated with these modes are expected in the spectral region 1 240—650 cm^{-1}. The C–C stretching vibrations in the six-carbon-atom skeleton of this compound will give rise to two i.r. and three Raman frequencies. The strong mechanical coupling between each of the C–C vibrations in the skeleton and the coupling of the C–C stretching modes with the CH_3 rocking modes make the assignments of the C–C stretching and CH_3 rocking modes more difficult.[17,18]

(iii) C–NO_2 *Vibrations.*—The C–NO_2 group frequencies are assigned according to established group frequencies in standard texts and by correlations with the results of spectroscopic studies of simple aliphatic nitro compounds.[19–21] The nitro group is known to give strong absorptions in the 1 550 and 1 340 cm^{-1} region.[22] The correlation is confirmed by Raman data. We assign the bands at 1 553 and 1 540 cm^{-1} to the asymmetric stretching vibrations and those at 1 348 and 1 343 cm^{-1} to the symmetric stretching vibrations of the NO_2 group. The doublet at 857 and 853 cm^{-1} in the KBr pressed disc spectrum is assigned to the CN stretching vibrations. This assignment is reasonable because the dicyano and dimethyl analogues of this compound, having no CN stretching modes, should not have any such bands in their spectra and this is true for the spectra of these two compounds as they do not have any bands in the 870—800 cm^{-1} region. The band at 648 cm^{-1} has been assigned to the bending mode of the nitro group. This assignment is tentative as this band could also be attributed to a C–C stretching mode involving non-central as well as central carbon atoms. The NO_2 group rocking modes have not been identified with any obvious frequency in view of the variabilities normally associated with them. No doubt they would couple with some of the skeletal deformation modes involving the central and methyl groups.

(iv) *Skeletal Deformation Modes*.—Modes like C–C–C bending, rocking, wagging, and twisting occur in the frequency region 600—430 cm^{-1} and have been assigned as such in Table 1.

Comparison of Solid- and Liquid-phase Spectra.—Inspection of the i.r. spectra of the solid shows that the KBr pressed disc spectrum is similar to those of the mulls. This rules out any possibility of the compound undergoing internal rotation during the process of pressing as was found for 2,3-dibromo-2,3-dimethylbutane by Park and Wyn-Jones.[13] The solution i.r. spectra show the presence of four extra bands, compared with the solid state spectra. The additional bands at 495, 598, and 890 cm^{-1} are observed in all the solvents used while the 843 cm^{-1} band is observed only in benzene. A logical interpretation of the existence of extra bands is that the solution state contains more different rotational isomers than the solid state.

Comparison of the Raman and i.r. spectra of solid 2,3-dinitro-2,3-dimethylbutane shows that the conformation of the molecule in the solid state is one which does not possess a centre of symmetry. The *gauche*-rotamer thus seems to predominate in the solid. The extra bands in solution are thus assigned to the *trans*-rotamer. The assignment is also supported by the fact that the extra bands at 495, 598, and 890 cm^{-1} decrease in intensity with increasing dielectric constant of the solvent. Especially significant is the marked decrease in intensity of the 495, 598, and 890 cm^{-1} bands in acetonitrile solution, showing the small proportion of the *trans*-rotamer in this very polar solvent. Were these bands due to the *gauche*-rotamer, they would increase in intensity with increasing dielectric constant of the solvent, not decrease, as is observed.

The extra band at 495 cm^{-1} could be due to the symmetrical C–C–C deformation of the *trans*-rotamer. The corresponding band for the *gauche*-isomer is probably at 513 cm^{-1}. It is interesting to observe the behaviour of some of these bands in the solid and solution states. In the solid, two bands, 525 and 513 cm^{-1}, which are due to the *gauche*-isomer, are quite strong but on dissolution in CS_2 or CCl_4 the 525 cm^{-1} band decreases in intensity while the 513 cm^{-1} band seems to have disappeared. Probably it is so weak as to be masked by other bands. Instead a band at 495 cm^{-1} appears. In acetonitrile solution, the 513 cm^{-1} band reappears and the two bands at 521 and 511 cm^{-1} in acetonitrile resemble the two bands in the solid. Also the extra *trans* band at 495 cm^{-1} has decreased in intensity and appears as a shoulder at 493 cm^{-1} to the 511 cm^{-1} band in this very polar solvent. This confirms the low proportion of the *trans*-rotamer in a polar solvent.

The extra band at 598 cm^{-1} could be another symmetric C–C–C deformation fundamental of the *trans*-form. The corresponding band for the *gauche*-form would be at 570 cm^{-1}. On dissolution in CCl_4 and CS_2, this *gauche*-band decreases in intensity showing the decrease of the proportion of the *gauche*-rotamer in these two non-polar solvents. Moreover, the intensity of this band increases with increasing dielectric constant of the solvents. The marked increase in acetonitrile confirms that it is a vibration due to the *gauche*-rotamer. The relative intensities of these two bands give a rough idea of the *gauche*-*trans* ratio in solution. In CCl_4 and CS_2 solutions the 570 cm^{-1} band appears only as a strong shoulder to the 598 cm^{-1} band, indicating that the *gauche*-isomer is in smaller proportion compared with the *trans*. However, this 570 cm^{-1} band increases in intensity relative to the 598 cm^{-1} band in benzene and $CHCl_3$ showing that the *gauche* population has increased until, in acetonitrile, the relative intensities of the two bands are reversed showing that the *gauche*-rotamer now predominates. The extra band at 890 cm^{-1} in all the solvents is attributed to a mixture of CH_3 rocking and C–C stretching modes. As mentioned earlier, the intensity of this band decreases with increasing polarity of the solvent, showing that it is a band due to the *trans*-rotamer.

The extra band at 843 cm^{-1} in benzene solution is due to the CN stretching vibration of the *trans*-rotamer. The corresponding band of the *gauche*-rotamer is probably at 848 cm^{-1}. The extra *trans* band at 843 cm^{-1} is not seen in acetonitrile solution probably because it is too weak to be observed and not seen in the other less polar solvents probably because it coincides with the *gauche* bands.

Although all the bands of the solid are *gauche* bands, it is interesting to note that these bands do show differences in character in the different solvents. Many of the *gauche* bands decrease in intensity on dissolution of the solute in non-polar solvents but increase in intensity with increasing polarity of the solvents. Such bands in solution are thus purely *gauche* bands as are the following bands: 513, 525, 570, 648, 683, 768, 853, 857, 1 017, 1 136, 1 140, 1 222, 1 240, 1 413, 1 439, 1 473, and 3 035 cm^{-1}. It is interesting to observe two CN stretching vibrations at 857 and 853 cm^{-1}. On dissolution in CS_2 and CCl_4, the 853 cm^{-1} band decreases in intensity while the 857 cm^{-1} band seems to disappear. Probably it is so weak that it cannot be observed. However, this band reappears in the solvents of higher dielectric constant like benzene, chloroform, and acetonitrile while the 853 cm^{-1} band increases in intensity steadily.

Besides the purely *gauche* bands, there are some bands in solution which remain fairly constant in intensity in the different solvents. These bands must be due to the extra *trans* bands coinciding with *gauche* bands. In non-polar solvents, the *gauche* intensity decreases but the *trans* bands do make substantial contributions to these *gauche* bands and the overall effect would be to cause these bands to appear approximately constant in intensity. Such bands attributed to a mixture of rotamers are at 435, 735, 950, 1 174, 1 343, 1 384, 1 398, and 3 010 cm^{-1}. It is also noteworthy that in the Raman spectra of $CHCl_3$ solution an extra band is observed at 826 cm^{-1}, attributable to the *trans*-rotamer.

Thus from the i.r. and Raman spectra of the compound in the solid state, the very few extra lines in solution and the behaviour of the bands in the solution states, we conclude that the *gauche*-rotamer predominates in the solid state while a mixture of rotamers is present in solution, the *trans* predominating in the less polar solvents like CCl_4 and CS_2 and the *gauche* increasing in proportion as the polarity of the solvent increases.

It is interesting to note that Fitzgerald and Janz[3] used a somewhat similar reasoning to conclude that below −43.7 °C only the *gauche*-rotamer of succinonitrile is present, while above this temperature, both the *trans*- and *gauche*-rotamers coexist. They based their argument on the fact that only four bands disappeared on cooling below −43.7 °C. They felt that, in a system in which the *trans*-rotamer has the lower energy, the i.r. spectral simplification would be much greater since the *gauche*-rotamer has twice as many i.r.-active modes as the *trans*.

Other Studies on 2,3-*Dinitro*-2,3-*dimethylbutane*.—Diallo[23] has studied the i.r. spectra of this compound in the solid and solution states. However, the number of bands reported by him are less than those observed by us in the same spectral region and he has not mentioned the bands in the 800—400 cm^{-1} region which is of some relevance to rotational isomerism, as our earlier discussion shows. Consideration of the selection rules for the C–N vibrational modes led to the conclusion that there should be one such active band for the *trans*-rotamer (C_{2h}) and two bands for the *gauche*-rotamer (C_2). Since the observed spectra contained two C–N frequencies, at 850 and 843 cm^{-1}, it was concluded that this was consistent with the existence of 2,3-dinitro-2,3-dimethylbutane in the *gauche* conformation in the solid state, although an alternative interpretation in terms of a mixture of *trans–gauche* isomers is possible, if it is assumed that two C–N fundamental frequencies (one for each isomer) coincide. The fact that the relative intensity of the high-frequency band varies with temperature, but not the lower-frequency band, was also cited as evidence in favour of the two bands as being due to a type-B vibration and type-A vibration respectively of the *gauche*-rotamer, and not as the result of redistribution of rotational isomers. However, it was realised that these findings needed to be confirmed by Raman data. Our Raman and i.r. spectra do confirm that in the solid state the compound does not have any centre of symmetry and is in the *gauche*-form.

From another independent dielectric study of the dinitro compound, Wright[24] was able to conclude that the rotamer present in the crystal is not likely to be the *trans*. This is because his measurement of the distortion polarisation of the dinitro compound in the solid indicated that the atomic polarisation was anomalously high and this was possible only if the rotamer in the solid was in the *gauche*-form.

Dipole Moment and Kerr Effect Measurements.—Results of the polarisation measurements of 2,3-dinitro-2,3-dimethylbutane in benzene at 25, 45, and 60 °C and in CCl_4 at 5, 25, and 45 °C, in cyclohexane at 25 °C, and in dioxane at 25 °C, are summarised in Table 3. Kerr effect measurements in benzene and carbon tetrachloride are also recorded there.

The dipole moment of 2-nitropropane, being needed in the calculations for the dipole moment of the different conformations of the dinitro compound, has also been measured in CCl_4 and benzene at 25 °C. Results are included in Table 3.

Calculation of Dipole Moment and Kerr Constants.—For a symmetrically 1,2-disubstituted ethane $YCR_2–CR_2Y$, the resultant moment $\mu(\theta)$ of any conformation can be shown[25] to be given by equation (1) where μ_0 is the moment of the symmetrical

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

half (CR_2Y) of the molecule, α is the supplement of the C–C–Y bond angle, and 2θ is the dihedral angle between the two C–C–Y planes. For 2,3-dinitro-2,3-dimethylbutane, the C–C–NO_2 angle may be taken as 110°. In our calculation of the dipole moment of the various conformations, μ_0 is taken to be the dipole moment of 2-nitropropane in the same solvent in which the molar Kerr constants are determined and its direction along the C–NO_2 bond. α Is assumed to be 70°; errors arising from this assumption are probably negligible since simple calculations show that a deviation of ±2° from tetrahedral symmetry causes only *ca.* 1—2% change in $\mu(\theta)$.

For an equilibrium mixture of N_t molecules in the *trans*-conformation having dipole moment μ_t and N_g *gauche*-rotamers of dipole moment μ_g, it can be shown[26] that the mean square dipole moment of the mixture is given by equation (2).

$$\bar{\mu}^2 = \frac{\mu_t^2 N_t + \mu_g^2 N_g}{N_t + N_g} \qquad (2)$$

The root mean square moment $\bar{\mu}$ can be equated to the observed moment (μ_{obs}). The moment of the *trans*-rotamer μ_t (where 2θ = 180°) can be taken as zero because although μ_t might have a small finite value due to slight torsional oscillations about the central C–C bond, the magnitude is too low to cause significant differences in the final results.[27] Substituting $\bar{\mu}^2 = \mu^2_{obs}$ and $\mu_t = 0$ in equation (2) gives $\mu^2_{obs} = \mu_g^2 N_g/(N_t + N_g)$.

The *gauche* conformer population x% is then given by equation (3). Since μ_g is a function of θ, x is also dependent on θ.

$$x = \frac{100N_g}{N_g + N_t} = \frac{100\mu^2_{obs}}{\mu_g^2} \qquad (3)$$

The molar Kerr constant ${}_mK$ of any conformation can be calculated as a function of the dihedral angle using the appropriate bond and group polarisabilities. This enables the mean molar Kerr constant $\overline{{}_mK}$ of an equilibrium mixture of *gauche*- and *trans*-conformers to be calculated *via* equation (4).[25] In our calculation of the molar Kerr constants for the

$$\overline{{}_mK} = \frac{{}_mK_tN_t + {}_mK_gN_g}{N_t + N_g} \qquad (4)$$

various conformations, the rectangular axes to which the bond–group polarisabilities and moments are resolved are: the X axis along the C–C bond, the Y axis perpendicular to one of the C–C–Y planes, and the Z axis perpendicular to both these axes and lying in the plane containing C–C–Y. The bond and group polarisabilities (in units of 10^{-40} C m^2 V^{-1}) used are in Table 4. Again the mean molar Kerr constant can be equated to the observed ${}_mK$ value. Accordingly, X% can be expressed in terms analogous to equation (3) [equation (5)] and is also dependent on θ through ${}_mK_g$.

$$X = \frac{({}_mK_{obs} - {}_mK_t)}{({}_mK_g - {}_mK_t)} \times 100 \qquad (5)$$

Therefore from dipole moment and molar Kerr constant measurements, two separate plots of X% against dihedral angle can be obtained (Table 5). The point of intersection of these two

Table 4. Anisotropic polarisabilities of bonds and groups expressed by as 10^{-40} C m^2 V^{-1}

Bond–group	b_L	b_T	b_V	Ref.
C–H	0.72	0.72	0.72	28
C–C	1.09	0.29	0.29	28
C–NO_2	3.78	3.12	2.56	29
C–CH_3	3.23	2.45	2.45	28

Table 5. Calculated dipole moments and molar Kerr constants with corresponding *gauche* percentage population for various conformations of 2,3-dinitro-2,3-dimethylbutane

Dihedral angle (°)	0	50	80	85	90	93	102	180
$\mu_{(calc)}$	22.06	20.03	16.92	16.29	15.62	15.19	13.88	0
x%	20.7	25.2	35.2	38.0	41.4	43.8	52.3	
${}_mK_{(calc)}$	257.5	246.4	209.9	200.2	189.4	182.7	159.5	1.1
x%	30.5	31.9	37.5	39.4	41.6	43.1	49.4	

plots will give the $X\%$ and dihedral angle values which satisfy both the observed dipole moment and molar Kerr constant of the equilibrium mixture.

Evaluation of Dihedral Angle and gauche *Population.*—When the calculated values of percentage *gauche*-rotamer are plotted against the dihedral angle 2θ, it is seen that the observed dipole moment 10.04×10^{-30} C m and the molar Kerr constant (79×10^{-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° and 58% of the *trans*-rotamer. This substantiates, in more precise terms, our spectroscopic analysis which indicates that in a non-polar solvent such as CCl_4, the *trans* is of higher proportion.

On the other hand, the observed ${}_mK$ value in benzene is negative (-68×10^{-27} m^5 V^{-2} mol^{-1}), thus revealing a large solvent effect relative to carbon tetrachloride. Moreover, the calculated ${}_mK$ values for all the conformations are positive; thus the evaluation of the dihedral angle of the *gauche*-rotamer in benzene solution is not possible by this method in this case.

It is interesting to note that for 2,3-dicyano-2,3-dimethylbutane, the dipole moment in CCl_4 at 25 °C (7.11×10^{-30} C m) and molar Kerr constant (68×10^{-27} m^5 V^{-2} mol^{-1}) give 18% of the *gauche*-rotamer with a dihedral angle of *ca.* 85° and 82% of the *trans*-rotamer. The large dihedral angle value of 91° in CCl_4 for the dinitro compound can be explained in terms of the greater mutual repulsion of the bulkier nitro groups compared with the cyano groups, causing the nitro groups of the *gauche*-form to be pushed further apart. However, the greater *gauche* population compared with the dicyano compound shows that the energy difference between the *gauche*- and *trans*-rotamers for the dinitro compound is smaller than that between the *gauche*- and *trans*-rotamers in the dicyano compound. This is not surprising in view of the indications from our spectroscopic studies that the isomer present in the solid state of the dinitro compound is predominantly the *gauche*-rotamer. We have explained the stability of the *gauche*-form in terms of the stabilisation by its own reaction field in the close packing of the crystal lattice. No doubt in a non-polar solvent like CCl_4 this reaction field effect is reduced but still appears to be much greater than is the case with the dicyano compound. Since CCl_4 is isotropically polarisable and thus should yield inert solvent values of ${}_mK$, the dihedral angle of 91° and a *gauche* content of 42% can be considered to be the 'true' values for 2,3-dinitro-2,3-dimethylbutane.

The Internal Energy Difference between the Rotational Isomers, ΔE_s.—The internal energy difference between the rotational isomers (*i.e.* the *gauche* and *trans*) may be calculated from the Boltzmann-type equation (6). Thus ΔE_s may be

$$x/(1 - x) = N_g/N_t = 2 \exp(-\Delta E_s/RT) \qquad (6)$$

evaluated once the isomeric ratio is known.

With the use of this equation, ΔE_s for the dinitro compound is found to be 2.52 kJ mol^{-1}.

An alternative method of obtaining ΔE_s is to employ the temperature dependence of the dipole moment proposed by Lennard Jones and Pike.[30] From the temperature variation of the dipole moment in carbon tetrachloride, ΔE_s is found to be 2.48 kJ mol^{-1}. This is in good agreement with the value obtained by using dipole moment and Kerr constant measurements. Furthermore, the *gauche*-rotamer is found to have a dipole moment of 15.25×10^{-30} C m and a dihedral angle of 93°. As can be observed from Table 3, the variation of dipole moment in benzene follows a trend opposite to that in CCl_4. In benzene the dipole moment decreases with increasing temperature, showing that ΔE_s is negative. For the evaluation of a negative ΔE_s value, we plot a theoretical curve of $\ln g(x)$ against $\ln x$ where $g(x) = 1/[1 + 2\exp(-x)]$ and $x = \Delta E_s/RT$. The experimental curve of $\ln(\mu^2_{obs})$ *versus* $\ln(T)$ is superimposed on the theoretical curve and ΔE_s and μ_g obtained from the best fit.

From the experimental data for benzene solution, the internal energy difference between the two rotamers is found to be -1.67 kJ mol^{-1}. This corresponds to a composition of 79% *gauche* and 21% *trans* in solution. The dipole moment of the *gauche* rotamer is found to be 14.88×10^{-30} C m with a dihedral angle of 95°. Although this value for the dihedral angle of the *gauche*-isomer is slightly higher than that found in CCl_4, the difference is hardly distinguishable from experimental errors. It appears therefore that intermolecular interactions with the benzene solvent molecules do not affect the dihedral angle of the *gauche* conformer to any appreciable extent. Instead, intermolecular interactions seem to have increased the polarisation by increasing the *gauche* content. This is in agreement with the results for 2,3-dicyano-2,3-dimethylbutane which has been shown to have a dihedral angle of 85° in both CCl_4 and dioxane, although the dipole moment in the two solvents are very different. It should be noted that the value in CCl_4 was obtained using dipole moment and Kerr constant values at a specific temperature while that in dioxane, by the variation of the dipole moment with temperature. The Lennard-Jones and Pike method [30] seems to be useful for obtaining ΔE_s and the *gauche* dihedral angle even when strong intermolecular interactions occur between solute and solvent molecules, resulting in the molar Kerr constant value becoming strongly solvent dependent. When such interactions occur, the method of using the molar Kerr constant value to calculated ΔE_s and *gauche* dihedral angle leads to anomalous results. Thus the *gauche* dihedral angle of the dicyano compound was found to be 103° in benzene, a value significantly different from the value in CCl_4. However, the very failure of this method to give reasonable values for the dihedral angle and the *gauche* population shows also its very great sensitivity at detecting intermolecular interactions.

Solvent Effects.—Results of dipole moment measurements in different solvents show that there is a large solvent effect for this compound. The dipole moment in cyclohexane (9.81×10^{-30} C m), an 'inert' solvent, is not significantly different from that in CCl_4 (10.04×10^{-30} C m). However, as mentioned earlier, there is a large augmentation of dipole moment in benzene and dioxane relative to CCl_4 or cyclohexane. Moreover, the plots of solution dielectric constant against solute weight fraction for the benzene measurements at the three temperatures and for dioxane at one temperature show curvature. The observed concentration effects imply that the polarisation increases as the dielectric constant of the surrounding medium increases. The increase in polarisation with increasing solute concentration can be explained in terms of the stabilisation of the polar *gauche*-isomer by its own reaction field.[31] Our measurements of the dipole moment in benzene at different temperatures have shown that the increase in polarisation is not due to a change in dihedral angle of the *gauche*-conformer. However, stabilisation of the *gauche*-isomer to such an unusually high proportion could also be partly due to an additional factor, namely π-complex formation with the solvent benzene molecules. When dioxane is used as solvent, the augmentation in dipole moment (3.90×10^{-30} C m) relative to CCl_4 is greater than that in benzene (3.24×10^{-30} C m). For the dicyano compound, the dipole moment in dioxane at 25 °C is 9.74×10^{-30} C m, an increase of 2.64×10^{-30} C m relative to CCl_4, and this augmentation is also greater than that between benzene and CCl_4.

Since the dielectric constant of dioxane (ε_{25} 2.2090) is lower

Table 6. Thermodynamic quantities governing *gauche*/*trans* equilibrium in kJ mol^{-1}

Solvent	Temp. (°C)	$K = N_g/N_t$	$\Delta G°$	$\Delta H°$	ΔE
CCl_4	5	0.67	0.93	3.8 ± 0.7	2.52 ± 0.05
	25	0.76	0.68		
	45	0.84	0.46		
Benzene	25	3.93	−3.39	-2.7 ± 0.6	-1.67 ± 0.05
	45	3.65	−3.42		
	60	3.41	−3.40		

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

than those of benzene and CCl_4, stabilisation by the bulk dielectric constant of the solvent cannot be the sole factor.

Oi and Coetzee[32] have also noted this anomalous stabilisation of the *gauche*-conformer in dioxane in their i.r. studies on the rotational isomerism of 1,2-dichloroethane (DCE) and 1,1,2,2-tetrachloroethane (TCE). They concluded that interaction of DCE is mainly electrostatic in nature but, in the case of TCE, hydrogen bonding occurs significantly with proton-acceptor solvents. This would mean that in compounds where the hydrogen atoms present are 'acidic' as in TCE, hydrogen bonding with proton-acceptor solvents becomes important. As the nitro groups are even more strongly electron withdrawing, the hydrogen atoms present in the dinitro compound are more strongly acidic and the tendency to form hydrogen bonds with the electron-rich oxygen atoms of dioxane would be increased. Similarly, π-complex formation between benzene and the dinitro compound can occur through hydrogen bonding between the acidic hydrogen atoms and the π-electrons of benzene. As dioxane is known to be a better proton-acceptor solvent than benzene, this explains why the augmentation in dipole moment is greater in dioxane than in benzene as the interaction between dioxane and solute molecules is greater than that between benzene and the solute molecules. The preferential stabilisation of the *gauche*-rotamer as opposed to the *trans*-rotamer may be visualised as follows. In the *gauche*-configuration, the two nitro groups are closer together and constitute a 'field' which is negatively charged. The electron-rich oxygen atoms of dioxane or the π-electron cloud of benzene will avoid this site but they can interact with the hydrogen atoms of the four methyl groups without much hindrance by approaching the methyl groups from the region *away* from the two nitro groups. In the *trans*-configuration, the two nitro groups are separated and approach to the hydrogen atoms will be much more difficult.

This picture is consistent with the standard enthalpy values in Table 6 calculated from the equilibrium constants for the *trans* $\rightleftharpoons$ *gauche* equilibrium assuming $\Delta H°$ to be constant over the temperature range and using the Van't Hoff isochore. In carbon tetrachloride, the difference between $\Delta H°$ and ΔE [$\Delta H° = \Delta E° + \Delta(PV)$] is positive, implying that the process of converting the more stable *trans* into the *gauche* molecules is accompanied by an increase in volume, since the pressure remains constant. This is to be expected if there is no specific solute–solvent interaction and if we assume that the *gauche* rotamer, with lower symmetry, requires more space than the *trans*. On the other hand, in benzene solution, the difference between $\Delta H°$ and ΔE is negative implying a decrease in volume of the system when *trans* molecules are converted into the more stable *gauche*. Since the *gauche* molecules attract the solvent benzene molecules to form π-complexes more effectively than the *trans*, the net reduction in volume is explained.

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