

## Rotational Isomerism in 2,2,3,3-Tetranitrobutane

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I.r and Raman spectra of 2,2,3,3-tetranitrobutane (in solid and solution states) are reported and assignment of frequencies is made. Comparison of the Raman and i.r. spectra of solid and solution states shows that the compound exists as a mixture of *gauche*- and *trans*-rotamers in the solid, with the *gauche* predominating. Dipole moments in various 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, 2,2,3,3-tetranitrobutane exists as a rotameric mixture of 34% *gauche* and 66% *trans* in carbon tetrachloride solution, and 72% *gauche* and 28% *trans* in benzene solution. Solvent effects are also discussed.

Our interest in polar and steric effects on rotational isomerism in symmetrically substituted ethanes led us recently to investigate the influence of the nitro group in such molecules. The first paper<sup>1</sup> in this series showed that 2,3-dinitro-2,3-dimethylbutane exists in the *gauche*-conformation in the solid state, but as a mixture of 58% *trans* and 42% *gauche* rotamers in CCl<sub>4</sub> solution. We now report our findings on the related molecule 2,2,3,3-tetranitrobutane, based on dielectric, electric birefringence, and i.r. and Raman spectroscopic measurements.

### Experimental

**Solute.**—Our sample of 2,2,3,3-tetranitrobutane, prepared by a method described in the literature,<sup>2</sup> had m.p. 165–166 °C (decomp.) (Found: C, 20.3; H, 2.5; N, 23.8. Calc. for C<sub>4</sub>H<sub>6</sub>N<sub>4</sub>O<sub>8</sub>: C, 20.2; H, 2.5; N, 23.5%).

**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.<sup>3,4</sup>

**Apparatus.**—Kerr constants were measured photometrically;<sup>5</sup> dielectric constants were determined with a heterodyne-beat meter.<sup>6</sup> Densities and refractive indices were measured by standard procedures.<sup>7</sup>

Solid-state i.r. spectra were recorded for Nujol and hexachlorobutadiene mulls and for KBr disc samples. Solution-state spectra were obtained using solvents such as carbon tetrachloride, carbon disulphide, benzene, chloroform, and acetonitrile. A Perkin-Elmer 682 spectrophotometer was used for all these i.r. measurements. Raman measurements were made by 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.

### Results

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

**Fundamental Modes for the Rotamers.**—The *trans*-rotamer of C<sub>2h</sub> symmetry would have 17 A<sub>g</sub>, 14 A<sub>u</sub>, 13 B<sub>g</sub>, and 16 B<sub>u</sub> fundamentals; the *gauche*-rotamer of C<sub>2</sub> symmetry would have 31 A and 29 B fundamentals. Because of masking and overlapping, not all the expected frequencies would necessarily be observed. However, by examining the behaviour of a few

significant bands, it is possible to deduce the type of rotamer(s) present.

### Discussion

The assignment of bands for this compound follows that for 2,3-dinitro-2,3-dimethylbutane.<sup>1</sup> However, the characteristic NO<sub>2</sub> asymmetric stretching vibrations here are found as a single broad band at 1 600 cm<sup>-1</sup>, higher than those of most aliphatic nitro compounds. Three bands observed in the solid state at 847, 860, and 877 cm<sup>-1</sup> (in the region where C–N stretching vibrations are expected) appear to persist in benzene and acetonitrile solutions.

In his i.r. study of solid 2,2,3,3-tetranitrobutane, Diallo<sup>8</sup> pointed out that only two i.r.-active bands should be expected for the C–N vibrational modes of the *trans*-rotamer. Since three bands attributable to the C–N stretching vibrations instead of two were observed, Diallo<sup>8</sup> concluded that 2,2,3,3-tetranitrobutane exists as a mixture of *gauche*- and *trans*-conformers in the solid state, the additional band being due to the *gauche*-conformer. Our i.r. and Raman spectra of the solid and solutions of the compound not only confirm his conclusion but also suggest that the *gauche*-rotamer is present in higher proportion than the *trans* in the solid state and in solution in benzene and in polar solvents.

When the i.r. spectra for the solution state are compared with those for the solid state, no extra bands are seen. As an equilibrium mixture of rotamers is expected to exist in solution, it seems from the similarities of the solid- and solution-state spectra that, like the solution state, the solid state also consists of a mixture of *gauche*- and *trans*-rotamers. The *gauche*-conformation should introduce frequencies which are simultaneously active in both Raman and i.r. spectra. One group of frequencies, mutually exclusive in the Raman and i.r., might provide evidence for the existence of the C<sub>2h</sub> or *trans*-form. The second class of frequencies, allowed in both types of spectra, will be due to the other, less symmetric, *i.e.* *gauche*-conformer of C<sub>2</sub> symmetry. We are able to assign some of the observed frequencies to the different *gauche*- and *trans*-rotamers by observing the behaviour of these bands in solution.

In the non-polar solvents carbon disulphide and carbon tetrachloride, we expect in general an increase in the intensity of the *trans*-bands and a corresponding decrease in the intensity of the *gauche*-bands. However, in a very polar solvent like acetonitrile, the situation is reversed and we might expect the *gauche*-bands to increase in intensity.

Table 1 shows the i.r. and Raman spectra of the compound in the solid state as well as in various polar and non-polar solvents. The spectral listings make for easy comparison of

Table 1. I.r. and Raman spectra of 2,2,3,3-tetranitrobutane in the solid and solution states<sup>a</sup> (concentrations of solutions are given in weight %)

Nujol	C <sub>4</sub> Cl <sub>6</sub>	KBr	CCl <sub>4</sub> (2.4%) (ε <sub>20</sub> 2.238)	CS <sub>2</sub> (1.7%) (ε <sub>20</sub> 2.641)	C <sub>6</sub> H <sub>6</sub> (4.4%) (ε <sub>20</sub> 2.284)	CHCl <sub>3</sub> (3.0%) (ε <sub>20</sub> 4.806)	CH <sub>3</sub> CN (4.2%) (ε <sub>20</sub> 37.5)	Raman solid	Raman CCl <sub>4</sub>	Approximate group assignment
3 040 (19)	3 045 (27)	3 050 (26)	3 043 (21)	3 042 (16½)	x	3 035 (8)	x	3 054 (13)	3 050 (0.70)	ν(CH <sub>3</sub> )(as)
x	2 970 (15)	2 980 (25)	2 990 (3)	2 990 (2½)	x	2 990 (2½)	x	2 980 (1.70)		
x	2 930sh(2)	2 930sh(2)	2 965 (3½)	2 965 (4)	2 955sh (3)	2 965 (6)	x	2 979 (26½)		
x	2 930sh(2)	2 930sh(2)	2 930 (10)	2 930 (10)	2 930 (17)	2 935 (13)	x			ν(CH <sub>3</sub> )(sym)
x	2 895 (31)	2 910 (32)	2 890 (36)	2 890 (36)	2 890 (20)	2 895 (49)	x			
2 650 (5½)	2 650 (11)	2 650 (14)	2 635 (14)	2 635 (10½)	2 640 (8)	2 640 (24)	2 650 (14)			2 × δ(CH <sub>3</sub> )(sym)
2 615 (2)	2 615 (2)	2 615 (6)	2 600 (3½)	2 600 (3)	2 610 (3)	2 610 (4)	2 630sh (3)			
1 595br (53)	1 595br (65)	1 595vbr (46)	1 595br (59)	1 610 (45)	1 585br (39)	1 595br (69)	1 605 (75)	1 621 (3)	1 600 (1.15)	ν(NO <sub>2</sub> )(sym)
								1 601 (15)		
								1 594 (2)		
1 463sh (1½)	1 454sh (1½)	1 457 (4)	1 450sh (½)	x	x	1 450 (2)	x	1 585 (1½)		δ(CH <sub>3</sub> )(as)
1 445br (44½)	1 445 (50)	1 450 (40)	1 440 (47)	x	1 440 (30)	1 440 (62)	x	1 462 (4½)	1 450 (0.70)	
								1 447 (9½)	1 400 (0.90)	δ(CH <sub>3</sub> )(sym)
1 399 (37)	1 402 (43)	1 409 (5)	1 392 (48)	1 386 (54)	x	1 400 (½)	x	1 406 (14½)		
1 388 (8)	1 389 (3)	1 391 (5)	1 385 (2)	x	1 395 (13)	1 394 (30)	x	1 393 (3½)		
	1 345 (1)	1 350 (16)	1 345 (2)	1 342sh (1)	1 383 (7)	1 385 (30)	x	1 438 (3½)		ν(NO <sub>2</sub> )(sym)
1 341 (36)	1 340 (51)	1 343 (11)	1 335 (38)	1 339 (62)	1 345sh (2)	1 347 (3)	x	1 438 (3½)		
					1 340br (24½)	1 337 (33)	x	1 406 (14½)		
1 312 (36)	1 310br (38)	1 315br (23)	1 305br (23)	1 305br (48)	1 305br (17)	1 308br (18)	1 295 (36½)	1 357 (21)	1 355 (1.40)	ν(NO <sub>2</sub> )(sym)
1 210 (5½)	1 212 (9½)	1 215 (15½)	1 210 (3)	1 212 (4)	1 210 (4½)	x	1 212 (11½)	1 318 (16)	1 320 (1.40)	
1 153 (3)	x	1 157 (4½)	1 160sh (2)	1 155sh (2)	1 148sh (3)	1 156 (3½)	1 156 (6)	1 314 (2)	1 160 (0.40)	ν(C-C) and p(CH <sub>3</sub> )
								1 159 (4)	1 130 (0.40)	
1 120 (52)	1 120 (56)	1 125 (68)	1 125 (55)	1 125 (75)	1 122 (37)	1 125 (63½)	1 122 (72)			ν(C-N)
		1 119 (2)				1 120 (1½)				
1 083 (15)	1 083 (19)	1 087 (15)	1 088 (12)	1 088 (12)	1 082 (10)	1 086 (15)	1 083 (7)			ν(C-C) and p(CH <sub>3</sub> )
1 067 (2)	1 067 (3½)	1 068 (4½)	1 055 (13)	1 056 (14)	x	1 055 (8½)	x	930 (15½)	930 (0.80)	
925 (1½)	925 (½)	928 (7½)	926 (1)	925 (1)	925 (½)	920 (1)	910 (9)	879 (6)	890 (0.35)	ν(C-N)
								870 (8)	870 (0.60)	
871 (10½)	870 (5)	877 (2)	868 (4)	865sh (8)	873 (3)	865 (59)	872 (5)			ν(C-C) and p(CH <sub>3</sub> )
857 (53)	x	860br (57)	850 (57)	848 (75)	860 (28)	865 (59)	860 (71)			
845 (8)	x	847sh (2)	x	x	840 (1½)	845br (3)	845 (6)			ν(C-N)
795sh (2½)	x	799sh (3)	x	794 (27½)	792 (2)	x	795sh (2)	850 (51½)	850 (2.40)	
784 (37)	784 (59)	788 (46½)	x	783 (48½)	780 (2)	x	785 (58½)			ν(C-C) and p(CH <sub>3</sub> )
776 (5)	775sh (3)	778sh (2)	x	775sh (2)	775sh (1½)	x	778sh (2)	781 (9½)	780 (1.00)	
x	703 (25½)	744 (38)	x	739 (11)	x	x	743 (7)			ν(C-C) and p(CH <sub>3</sub> )
703 (9½)	703 (24)	707 (36)	700 (17)	703 (10½)	x	x	704 (30)	751 (4)		
690sh (½)	690sh (½)	695sh (½)	x	690sh (1½)	x	x	695sh (2)	709 (7½)		pNO <sub>2</sub>
648 (12)	x	653 (32)	642 (26)	643 (21)	x	x	649 (26)	697 (7½)	695 (0.45)	
599 (17)	600 (30)	600 (37)	595 (37)	598 (38)	597 (27½)	597 (38)	597 (31)	599 (5)	590 (0.10)	δ(C-C-C)
528 (15½)	528 (28)	532 (43)	525 (4)	525 (5)	526 (6)	525 (11½)	527 (34)	530 (14)	526 (0.75)	
500 (4)	502 (6)	507 (7½)	496 (29)	497 (27)	498 (17½)	495 (40)	500 (7)	507 (28)	501 (1.30)	

<sup>a</sup> x indicates masking by background solvent or mulling agent; numbers in parentheses indicate relative intensities.

**Table 2.** Polarisation, refractions, dipole moments, and molar Kerr constants at infinite dilution of 2,2,3,3-tetranitrobutane. Incremental changes in the relative permittivities, densities, refractive indices, and Kerr constants ( $\Delta\epsilon$ ,  $\Delta d$ ,  $\Delta n$ , and  $\Delta B$ , respectively) were measured for solutions having solute weight fractions  $w_2$ . The coefficients  $\alpha$ ,  $\beta$ ,  $\gamma$ , and  $\delta$  were derived from the relations  $\alpha\epsilon_1 = \Sigma\Delta\epsilon/\Sigma w_2$ ,  $\beta d_1 = \Sigma\Delta d/\Sigma w_2$ ,  $\gamma n_1 = \Sigma\Delta n/\Sigma w_2$ , and  $\delta B_1 = \Sigma\Delta B/\Sigma w_2$ . When the plots  $\Delta\epsilon$  versus  $w_2$  showed curvature, as in the case of benzene,  $\text{CCl}_4$ , and dioxane solutions, a regression formula of the type  $\Delta\epsilon = aw_2 + bw_2^2$  was used to fit each experimental curve and the coefficients  $a$  and  $b$  were determined;  $\alpha$  was then derived from  $\alpha\epsilon_1 = a\epsilon_1(mK_2)$  refers to the solute molar Kerr constant at infinite dilution

Temp. (°)	Solvent	Concn. range ( $10^5 w_2$ )	$\alpha\epsilon_1$	$\beta$	$\gamma$	$\delta$	$P_2/\text{cm}^3$	$R_D/\text{cm}^3$	$10^{30}\mu^a/\text{Cin}$	$10^{27}\epsilon_1(mK_2)/\text{m}^5\text{V}^{-2}\text{mol}^{-1}$
25	$\text{C}_6\text{H}_6$	789—5 264	6.56	0.454	-0.009	-2.92	338.0	41.7 <sup>b</sup>	12.64 ± 0.03	-109 ± 2
45	$\text{C}_6\text{H}_6$	586—5 174	5.62	0.454			307.3		12.31 ± 0.03	
60	$\text{C}_6\text{H}_6$	995—8 331	5.02	0.461			286.7		12.11 ± 0.03	
5	$\text{CCl}_4$	435—1 241	6.17	-0.053			196.0		8.74 ± 0.03	
25	$\text{CCl}_4$	730—1 653	5.81	-0.042	0.010	30.24	192.1	43.9	8.91 ± 0.07	68 ± 6
45	$\text{CCl}_4$	508—1 861	5.62	-0.026			192.8		9.24 ± 0.03	
25	$\text{C}_6\text{H}_{12}$	763—1 331	2.20	0.478			166.4	43.2	8.11 ± 0.10	
25	$\text{C}_4\text{H}_8\text{O}_2$	709—5 994	10.12	0.345			439.4	43.3	14.65 ± 0.03	

<sup>a</sup> Calculated on the basis that  $\rho P = 1.05 R_D$ . <sup>b</sup>  $R_D(\text{calc.}) = 43.3 \text{ cm}^3$ .

relative band intensities. For instance, of the two bands at 532 and 507  $\text{cm}^{-1}$  in the solid state the band at 532  $\text{cm}^{-1}$  is of greater intensity. In the non-polar solvents carbon disulphide and carbon tetrachloride, this band decreases in intensity, while the 507  $\text{cm}^{-1}$  band remains approximately constant in intensity. In the polar acetonitrile solvent, the 532  $\text{cm}^{-1}$  band increases in intensity, becoming more intense than the 507  $\text{cm}^{-1}$  band. These facts suggest that the 532  $\text{cm}^{-1}$  band can be assigned to the *gauche*-rotamer. Although the intensity of the 532  $\text{cm}^{-1}$  band is given as (4) in carbon tetrachloride (appearing at 525  $\text{cm}^{-1}$ ) and as (6) in benzene (appearing at 526  $\text{cm}^{-1}$ ), the proportion of the *gauche*-rotamer in benzene compared with that in carbon tetrachloride could be considerably greater than that suggested by the ratio 4:6 if we allow for the fact that the intensities of common bands (e.g. at 1 125 and 850  $\text{cm}^{-1}$ ) in the two solvents are generally greater in carbon tetrachloride. Since the concentrations of solutes in different solvents have not been adjusted precisely to the same value, estimates of *gauche:trans* ratios from the intensities of any band in *different* solvents would not be as reliable as such estimates from dielectric data.

Another band of interest in the solid state is at 799  $\text{cm}^{-1}$ , where it appears as a strong shoulder to the band at 788  $\text{cm}^{-1}$ . In carbon disulphide it increases markedly in intensity, thus suggesting that it should be assigned to the *trans*-rotamer, which in a non-polar solvent would be expected to increase in proportion. This assignment is confirmed by the marked decrease of this band in the polar solvent acetonitrile, where the band is almost not observable.

Similarly, bands at 1 215, 1 157, 925, 877, 860, 778, and 707  $\text{cm}^{-1}$  have been found to decrease in intensity in carbon disulphide and carbon tetrachloride but to increase in intensity in acetonitrile. These may therefore be assigned to the *gauche*-rotamer. On the other hand, the band at 1 068  $\text{cm}^{-1}$  has been assigned to the *trans*-rotamer. From the relatively weak intensity of this band and the other *trans*-band at 799  $\text{cm}^{-1}$  mentioned earlier, we can conclude that in the solid state the proportion of *gauche*-rotamer present is greater than that of the *trans*-form.

A comparison of the i.r. and Raman spectra of the solid shows that the *gauche*-frequencies in the i.r. spectra at 1 215, 1 157, ca. 930, 877, 860, 778, 707, and 532  $\text{cm}^{-1}$  are also present in the Raman spectrum except for that at 1 215  $\text{cm}^{-1}$ . This might be because this frequency is of too low an intensity to be observed. Typical *trans*-bands like those at 1 068 and 799  $\text{cm}^{-1}$  do not have their counterparts in the Raman spectrum.

Thus from the pattern of the i.r. bands in solution compared with those in the solid state, we are able to infer the presence of

both *gauche*- and *trans*-rotamers in the solid and solution states. The co-existence of these rotamers in the solid state has been confirmed by the fact that the identified *gauche*-bands can be found at the same frequencies in both Raman and i.r. spectra of the solid while the identified *trans*-frequencies are mutually exclusive in both Raman and i.r. spectra.

Our discussion so far has been based on the i.r. and Raman frequencies in the region 1 250—400  $\text{cm}^{-1}$ . The region of higher frequencies has not been discussed because the  $\text{CH}_3$  stretching,  $\text{NO}_2$  stretching, and  $\text{CH}_3$  deformation vibrations that occur in this region are usually not sensitive to conformational changes.

*Comparison with Analogues.*—We have compared our work on this compound with two very similar studies on the bromo- and chloro-analogues.<sup>9,10</sup> Solid 2,2,3,3-tetrabromobutane shows polymorphism, occurring in tetragonal and two orthorhombic forms. All the i.r. and Raman bands observed in the orthorhombic forms have also been observed in the tetragonal form, demonstrating their spectroscopic similarities. From a study of the C—Br and C—C stretching frequencies, it was concluded that, in the crystalline state, only the  $C_{2h}$  conformer is present.

The i.r. spectra of 2,2,3,3-tetrachlorobutane were obtained over the temperature range +180 to -170 °C. No simplification of the spectra was observed as the temperature was lowered. Comparison with the Raman spectra of the solid showed that two categories of frequencies were present. Frequencies in one group were simultaneously present in the Raman and i.r. spectra and were assigned to the *gauche*-rotamer. Frequencies in a second group were mutually exclusive in the two types of spectra and were assigned to the *trans*-rotamer. It was thus concluded that the tetrachloro-compound exists as a mixture of rotamers in the solid state. This is very similar to the behaviour of 2,2,3,3-tetranitrobutane.

It is interesting to compare 2,3-dinitro-2,3-dimethylbutane with 2,2,3,3-tetranitrobutane, and 2,3-dichloro-2,3-dimethylbutane with 2,2,3,3-tetrachlorobutane from the point of view of the relative stabilities of the *trans*- and *gauche*-conformers in the solid state. 2,3-Dinitro-2,3-dimethylbutane exists in the *gauche*-conformation in the solid state. With the introduction of two bulky nitro groups in place of two methyl groups to give 2,2,3,3-tetranitrobutane, the *gauche*-rotamer becomes less stable with respect to its *trans*-counterpart. Thus in the solid state, instead of existing in the *gauche*-form only, 2,2,3,3-tetranitrobutane exists as a mixture of rotamers, but with the *gauche*-rotamer still predominating. In contrast, 2,3-dichloro-2,3-dimethylbutane exists as a mixture of *trans*- and *gauche*-forms in the high-

**Table 3.** Thermodynamic quantities governing *gauche/trans* equilibrium (in kJ mol<sup>-1</sup>) for 2,2,3,3-tetranitrobutane<sup>a</sup>

Solvent	Temp. (°C)	$K = N_g/N_t$	$\Delta G^\circ$	$\Delta H^\circ$	$\Delta E$	$\Delta H^\circ - \Delta E$
CCl <sub>4</sub>	5	0.49	1.65			
	25	0.52	1.62 (0.68) <sup>b</sup>	3.1 ± 0.9 (3.8 ± 0.7)	3.35 ± 0.4 (2.52 ± 0.1)	-0.3 ± 0.9 (1.3 ± 0.7)
	45	0.58	1.44			
Benzene	25	2.60	-2.37 (-3.39)			
	45	2.17	-2.05 (-3.65)	-6.5 ± 0.2 (-2.7 ± 0.6)	-0.64 ± 0.4 (-1.67 ± 0.1)	-5.8 ± 0.5 (-1.0 ± 0.6)
	60	1.96	-1.86			

<sup>a</sup>  $\Delta G^\circ$  is calculated from the relation  $\Delta G^\circ = -RT \ln K$ ;  $\Delta H^\circ$  is obtained from the slope of the  $\ln K$  versus  $1/T$  plot by the method of least squares and assuming  $\Delta H^\circ$  to be constant over the temperature range. <sup>b</sup> Numbers in parentheses refer to corresponding values for 2,3-dinitro-2,3-dimethylbutane.

temperature solid phase with the *trans*-form having lower energy than the *gauche*.<sup>11</sup> When two methyl groups are replaced by two chloro groups to give 2,2,3,3-tetrachlorobutane, both rotamers are approximately of equal energy.

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

The dipole moment increases with increasing temperature in carbon tetrachloride. This shows that  $\Delta E_s$  is positive and that the *trans*-rotamer is more stable than the *gauche* in this solvent. By the Lennard-Jones-Pike method,<sup>12</sup>  $\Delta E_s$  is evaluated as  $3.35 \pm 0.4$  kJ mol<sup>-1</sup>, with the dipole moment of the *gauche*-rotamer ( $\mu_g$ ) equal to  $15.25 \times 10^{-30}$  Cm and the torsion angle 83°. These values correspond to a *gauche*-rotamer population of 34% in carbon tetrachloride. Our spectroscopic results, which show that in a non-polar solvent the *trans*-rotamer predominates over the *gauche*, are in broad agreement with this value. The larger  $\Delta E_s$  value of 2,2,3,3-tetranitrobutane (3.35 kJ mol<sup>-1</sup>) compared with that of 2,3-dinitro-2,3-dimethylbutane (2.48 kJ mol<sup>-1</sup>) shows that replacement of two methyl groups by two nitro groups has made the *gauche*-rotamer of the tetranitro compound less stable than that of the dinitro compound in carbon tetrachloride solution, probably because of greater steric and repulsive interactions.

Like 2,3-dinitro-2,3-dimethylbutane,<sup>1</sup> the dipole moment of 2,2,3,3-tetranitrobutane in benzene decreases with increasing temperature. This indicates once again that  $\Delta E_s$  is negative and that in benzene the *gauche*-rotamer is now the more stable rotamer. Calculations show that  $\Delta E_s$  has a value of  $-0.64 \pm 0.4$  kJ mol<sup>-1</sup> with  $\mu_g$  equal to  $14.88 \times 10^{-30}$  Cm and the torsion angle 86°. The *gauche*-rotamer population corresponding to these values is then calculated to be 72%. This value for the torsion angle agrees quite well with that found when carbon tetrachloride is the solvent. This suggests that the interaction between 2,2,3,3-tetranitrobutane and the benzene solvent molecules does not affect the molecular parameters of the solute molecules. The augmentation in dipole moment of the compound in benzene relative to carbon tetrachloride may thus be attributed to an increase in *gauche*-content only.

As in 2,3-dinitro-2,3-dimethylbutane,<sup>1</sup> differences in dipole moments are observed when the solvent is changed. The dipole moment in cyclohexane ( $8.11 \pm 0.10 \times 10^{-30}$  Cm) is somewhat smaller than that in carbon tetrachloride at 25 °C ( $8.91 \pm 0.07 \times 10^{-30}$  Cm). This is probably due to the smaller dielectric constant of cyclohexane (2.020), which produces a smaller 'reaction field'<sup>13</sup> at the solute molecule. It is interesting that in

carbon tetrachloride (as well as benzene and dioxane), the plot of dielectric constant of the solutions against solute concentration shows curvature. This indicates that there is a non-linear self-enhancing effect here in that as the concentration increases, thus increasing the dielectric constant of the surrounding medium, the polar *gauche*-rotamer becomes progressively more stabilised by its own reaction field, resulting in a progressively increasing shift in the *gauche/trans* equilibrium in favour of the *gauche*-rotamer. In cyclohexane, however, this is not observed and only a straight-line plot is obtained.

In benzene, there is a large augmentation in the dipole moment with respect to carbon tetrachloride at 25 °C ( $3.73 \times 10^{-30}$  Cm). In this case, since the dielectric constants of carbon tetrachloride and benzene are similar in value (2.227 and 2.273, respectively) the reaction field effect will be similar. It seems more likely that the augmentation is due to  $\pi$ -complex formation between the solute and benzene solvent molecules. In agreement with this, the molar Kerr constant value ( ${}_mK$ ) in benzene ( $-109 \pm 2 \times 10^{-27}$  m<sup>5</sup> V<sup>-2</sup> mol<sup>-1</sup>) is significantly different from that in carbon tetrachloride ( $68 \pm 6 \times 10^{-27}$  m<sup>5</sup> V<sup>-2</sup> mol<sup>-1</sup>) with  $\Delta_m K$  equal to  $-177 \times 10^{-27}$  m<sup>5</sup> V<sup>-2</sup> mol<sup>-1</sup>. The dipole moment of the compound in dioxane at 25 °C is  $14.65 \pm 0.03 \times 10^{-30}$  Cm. This gives an augmentation of  $5.74 \times 10^{-30}$  Cm with respect to carbon tetrachloride, far greater than a similar effect of  $3.90 \times 10^{-30}$  Cm in 2,3-dinitro-2,3-dimethylbutane. We have postulated that interaction between 2,3-dinitro-2,3-dimethylbutane and dioxane occurs through the 'acidic' hydrogen atoms of the compound with the electron-rich oxygen atoms of dioxane. A similar situation is expected to hold for 2,2,3,3-tetranitrobutane. In fact an n.m.r. study<sup>14</sup> has shown that the hydrogen atoms of the tetranitro compound are more 'acidic' than those of the dinitro compound. We should therefore expect stronger interaction between the solvent dioxane molecules and the solute, thus giving rise to a greater augmentation in dipole moment than in the dinitro compound.

It is worth mentioning here too that the augmentation of the dipole moment of the tetranitro compound in dioxane is greater than in benzene. This is again not surprising as dioxane is a better proton-acceptor solvent than benzene.

Table 3 gives free energy and enthalpy values for the *trans/gauche* equilibrium for 2,2,3,3-tetranitrobutane as well as some corresponding values for 2,3-dinitro-2,3-dimethylbutane (shown in parentheses for comparison). In carbon tetrachloride, the difference between  $\Delta H^\circ$  and  $\Delta E$  for 2,2,3,3-tetranitrobutane is small [ $\Delta H^\circ = \Delta E_s + \Delta(PV)$ ] though the experimental errors are such that it is difficult to say whether this difference is positive or negative. However, since the difference is small in absolute terms, we may conclude that there is little change in volume when the more stable *trans*-molecules are converted

into the *gauche* (the pressure remaining constant). This suggests that the degrees of interaction between the *trans*-rotamers and the solvent and between the *gauche*-rotamers and the solvent are comparable. By contrast, the difference between  $\Delta H^\circ$  and  $\Delta E$  in benzene solution is clearly negative, implying a decrease in volume of the system when *trans*-molecules are converted into the more stable *gauche*. This decrease in volume is consistent with our earlier suggestion that the *gauche*-molecules attract the solute benzene molecules to form  $\pi$ -complexes more effectively than the *trans*. The fact that the  $\Delta H^\circ - \Delta E$  for 2,2,3,3-tetranitrobutane ( $-5.8$ ) is much more negative than the corresponding value for 2,3-dinitro-2,3-dimethylbutane ( $-1.0$ ) suggests that  $\pi$ -complex formation takes place more effectively in the former compound.

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