Crystal and Molecular Structure of 2,4,6-Tribromo-1,3,5-trineopentylbenzene: Indications for Attractive Steric Effects in the Crystal

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The title compound crystallizes in the triclinic system, space group $P\bar{1}$, $a = 11.197(5)$, $b = 12.207(8)$, $c = 17.146(7)$ Å, $\alpha = 103.06(5)$, $\beta = 98.20(6)$, $\gamma = 91.08(3)°$. The structure was refined to R 0.068 6 for 4 816 independent reflections (X-ray diffractometer data). The unit cell contains two conformers in the ratio 1 : 1, one of which has all three neopentyl groups on the same side of the benzene ring, while the other has two on one side and one on the other. Indications for the operation of inter- and intra-molecular attractive steric effects are discussed.

DURING studies on the internal rotation of 1,3,5-trineopentylbenzenes (TNBs), it was found[1] that the slow-exchange ^1H and ^{13}C n.m.r. spectra of the trisubstituted compounds Cl_3TNB, Br_3TNB, and Me_3TNB could be consistently interpreted in terms of the predominance of a rotamer with all three neopentyl groups on the same side of the benzene ring. This was taken as evidence for the operation of attractive steric effects among the hydrocarbon residues in these molecules, an interpretation for which support was subsequently provided by molecular mechanics calculations[2] on various rotamers in TNB itself, Me_2TNB, and Me_3TNB.

We describe here the results of an X-ray crystallographic determination of the molecular structure of Br_3TNB, and attempt to extract from the data evidence for attractive steric effects. Both inter- and intramolecular aspects of the crystal structure are found to be interpretable in these terms.

EXPERIMENTAL

Crystal Data.—$C_{21}H_{33}Br_3$, $M = 483.17$. Triclinic, $a = 11.197(5)$, $b = 12.207(8)$, $c = 17.146(7)$ Å, $\alpha = 103.06(5)$, $\beta = 98.20(6)$, $\gamma = 91.08(3)°$, $U = 2\,256$ Å^3, $D_m = 1.47$, $Z = 4$, $D_c = 1.42$. Space group $P1$ (No. 1) or $P\bar{1}$ (No. 2), shown to be $P\bar{1}$ from structure analysis. Cu-$K_{\alpha 1}$ radiation, $\lambda = 1.540\,51$ Å; μ(Cu-$K_{\alpha 1}$) 75.0 cm^{-1}.

Intensity Measurements.—Unit-cell dimensions were determined from least-squares calculations on $\sin^2\theta$ values of 23 accurately centred reflections (Cu-$K_{\alpha 1}$ radiation).

Intensity data were collected on a computer-controlled four-circle CAD 4 diffractometer, equipped with a graphite monochromator (Cu-$K_{\alpha 1}$), by the ω—2θ scan technique with a scan interval $\Delta\omega = (0.80 + 0.50 \tan\theta)°$. Background was measured for one quarter of the scan time at each end of the interval. In the range $5 \leqslant \theta \leqslant 70°$, 8 959 reflections were registered of which 4 816 were considered observed, having $I > 3\sigma(I)$. The intensities of two control reflections were measured at regular intervals. Based on the resulting 358 values, the following scaling polynomial was deduced: $I_{corr} = I_{obs}(1 - 0.54 \cdot 10^{-3} \cdot h)$, where h is the number of hours of exposure of the crystal. The single crystal used had the shape of an oblique prism, the edges of which were parallel to the directions of the crystallographic axes. The lengths of the edges parallel to a, b, and c were 0.064, 0.225, and 0.110 mm, respectively. The resulting 4 618 reflections were corrected for Lorentz, polarization, and absorption effects.

Determinations and Refinement of the Structure.—Assuming space group $P\bar{1}$, all large maxima in a three-dimensional Patterson function could be explained as resulting from bromine–bromine vectors. The positions of the bromine atoms were refined by least-squares calculations, and a subsequent difference-Fourier map revealed all the carbon atom positions. The positions of the hydrogen atoms were not determined. In a final refinement, anisotropic temperature factors were introduced for the bromine atoms. The

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[1] R. E. Carter, B. Nilsson, and K. Olsson, *J. Amer. Chem. Soc.*, 1975, **97**, 6155.

[2] R. E. Carter and P. Stilbs, *J. Amer. Chem. Soc.*, 1976, **98**, 7515.

[3] L. Pauling, 'The Nature of the Chemical Bond,' Cornell University Press, New York, 1960, p. 260.

function minimized in the least-squares calculations was $\Sigma w(|F_o| - |F_c|)^2$, where $w^{-1} = \sigma^2(F_o^2)/4F_o^2 + 0.001\ F_o^2 + 4.0$.

Table 1

Final positional and isotropic thermal parameters for the non-hydrogen atoms of Br_3TNB, with estimated standard deviations in parentheses. Anisotropic temperature factors were used for the bromine atoms (see Supplementary Publication). The occupation numbers of atoms C(19′)—(21′) and C(19″)—(21″) were assumed to be 0.6 and 0.4

(*a*) Molecule (I)

Atom	*x*	*y*	*z*	$B/Å^2$
Br(2)	0.086 42(11)	0.184 41(13)	0.049 12(7)	(6.21)
Br(4)	0.012 60(11)	0.482 06(11)	0.339 48(8)	(6.04)
Br(6)	0.465 31(9)	0.297 03(12)	0.314 57(7)	(5.84)
C(1)	0.257 6(8)	0.229 0(8)	0.195 0(5)	3.98(18)
C(2)	0.137 2(8)	0.244 7(8)	0.162 6(5)	4.21(18)
C(3)	0.058 2(8)	0.311 5(8)	0.206 1(5)	3.96(18)
C(4)	0.106 1(8)	0.366 9(8)	0.284 0(5)	3.90(17)
C(5)	0.223 0(8)	0.357 5(8)	0.322 5(5)	4.13(18)
C(6)	0.295 3(8)	0.290 7(8)	0.273 4(5)	3.83(17)
C(7)	0.340 0(9)	0.154 8(9)	0.144 6(6)	4.58(20)
C(8)	0.343 0(9)	0.030 4(9)	0.149 8(6)	4.88(21)
C(9)	0.216 1(10)	−0.032 4(10)	0.125 0(7)	6.00(25)
C(10)	0.426 0(11)	−0.028 2(12)	0.089 9(8)	6.92(28)
C(11)	0.393 6(11)	0.015 9(11)	0.235 9(8)	6.82(28)
C(12)	0.267 9(8)	0.420 0(9)	0.410 5(6)	4.46(19)
C(13)	0.249 8(9)	0.356 9(9)	0.476 1(6)	4.56(19)
C(14)	0.295 0(11)	0.442 3(11)	0.558 9(8)	6.30(29)
C(15)	0.320 8(10)	0.249 7(10)	0.470 8(7)	6.02(25)
C(16)	0.115 8(11)	0.320 9(11)	0.474 4(7)	6.15(26)
C(17)	−0.071 8(9)	0.324 9(9)	0.168 5(6)	4.66(20)
C(18)	−0.170 3(10)	0.239 4(10)	0.179 8(6)	5.37(22)
C(19)	−0.150 0(12)	0.117 5(12)	0.138 3(8)	7.67(32)
C(20)	−0.177 2(13)	0.241 9(13)	0.269 7(9)	8.17(34)
C(21)	−0.292 0(15)	0.269 5(15)	0.137 2(10)	9.64(41)

(*b*) Molecule (II)

Atom	*x*	*y*	*z*	$B/Å^2$
Br(2′)	0.014 75(10)	0.589 82(12)	0.095 69(7)	(5.63)
Br(4′)	0.081 29(10)	1.000 83(10)	0.331 99(7)	(5.07)
Br(6′)	0.427 33(10)	0.669 45(12)	0.338 01(7)	(5.55)
C(1′)	0.216 4(7)	0.646 8(7)	0.220 8(5)	3.41(16)
C(2′)	0.103 3(7)	0.684 2(8)	0.192 4(5)	3.44(16)
C(3′)	0.053 4(7)	0.781 2(7)	0.226 7(5)	3.27(15)
C(4′)	0.126 6(7)	0.848 7(7)	0.295 2(5)	3.30(15)
C(5′)	0.233 3(7)	0.816 1(7)	0.334 1(5)	3.33(15)
C(6′)	0.274 6(7)	0.715 6(8)	0.293 4(5)	3.54(16)
C(7′)	−0.069 1(8)	0.817 4(8)	0.191 9(6)	4.25(18)
C(8′)	−0.180 4(9)	0.782 9(9)	0.227 2(6)	4.80(20)
C(9′)	−0.207 2(12)	0.656 5(12)	0.209 3(8)	7.19(30)
C(10′)	−0.290 7(15)	0.835 7(15)	0.189 5(10)	9.41(41)
C(11′)	−0.164 7(14)	0.826 4(14)	0.320 2(9)	8.94(38)
C(12′)	0.302 5(8)	0.887 5(8)	0.413 0(5)	4.03(18)
C(13′)	0.226 6(8)	0.866 7(8)	0.492 5(5)	4.18(18)
C(14′)	0.270 4(11)	0.743 8(11)	0.497 6(7)	6.49(27)
C(15′)	0.360 4(10)	0.937 6(10)	0.561 8(7)	5.97(25)
C(16′)	0.140 5(10)	0.907 6(10)	0.505 0(7)	5.92(25)
C(17′)	0.265 0(8)	0.537 8(8)	0.179 2(5)	4.04(18)
C(18′)	0.348 5(8)	0.543 3(8)	0.114 4(6)	4.16(18)
C(19′)	0.391 3(20)	0.661 3(20)	0.113 4(13)	6.9(5)
C(20′)	0.296 4(21)	0.464 4(22)	0.035 6(14)	7.5(5)
C(21′)	0.466 8(20)	0.485 3(20)	0.139 1(13)	7.2(5)
C(19″)	0.371 6(33)	0.417 1(33)	0.073 2(22)	8.0(8)
C(20″)	0.276 0(26)	0.574 9(26)	0.038 1(17)	6.0(6)
C(21″)	0.456 5(31)	0.621 4(30)	0.144 9(20)	7.1(8)

The final conventional *R* factor was 0.068 6 for 4 816 reflections. A restriction $0.5 \leqslant |F_o|/|F_c| \leqslant 2.0$ was used since some errors might have been introduced because of the needle connecting the crystal to the goniometer head being somewhat short. After subtracting the reflections outside the limits, *R* was 0.058 4 for 4 717 reflections. The goodness-of-fit, *S*, was 1.11. Final positional and isotropic thermal parameters are given in Table 1, and intermolecular distances in Table 2. Observed and calculated structure factors and isotropic thermal parameters are published in Supplementary Publication No. SUP 22238 (28 pp., 1 microfiche).*

RESULTS AND DISCUSSION

Molecular Conformations.—The asymmetric part of the unit cell of the present compound contains two molecules, (I) and (II), which are two possible different rotamers of a tri-substituted trineopentylbenzene [1,2] (see Figure 1). In molecule (I) [Figure 1 (a, b)], all three neopentyl groups are situated on the same side of the benzene ring, and the conformation is that expected for Br_3TNB from previous (solution) work [1]. In molecule (II) [Figure 1 (c, d)], two neopentyl groups are situated on one side of the ring plane, while the third is situated on the other side. The energy difference between molecules (I) and (II) in solution (corrected for symmetry effects) was estimated [1,2] to be of the order of 4 kJ mol^{-1} by n.m.r. measurements for $CDCl_3$ or CS_2 solutions at −10 to −20 °C; molecular mechanics calculations [2] on TNB and on Me_3TNB also resulted in an energy difference of *ca.* 4—5 kJ mol^{-1} between the rotamers corresponding to molecules (I) and (II). In view of the relatively small energy difference involved, the presence of equal amounts of molecules (I) and (II) in the crystal is perhaps not unduly surprising. It seems probable that the appearance of equal amounts of molecules (I) and (II) in the solid state may be attributed to an energy decrease associated with the packing of unlike molecules in the crystal structure (see later). We are thus provided by serendipity with a direct comparison of the molecular structures of the two possible rotamers in Br_3TNB, and,

Table 2

Intermolecular distances ⩽4.1 Å in the structure of Br_3-TNB. The sums of the van der Waals' radii (from ref. 3) are also given

(*a*) Contacts between molecule (I) and molecule (II) in the chain along the Y axis (see text)

$C(10^{I}) \cdots C(19')$	3.92(3)	4.0
$C(9^{I}) \cdots C(7')$	4.08(2)	4.0
$C(11^{I}) \cdots C(5')$	3.82(2)	3.7
$C(9^{I}) \cdots C(3')$	3.75(2)	3.7
$C(11^{I}) \cdots C(12')$	3.96(2)	4.0
$C(17) \cdots Br(2')$	3.87(1)	3.95
$C(4) \cdots C(17')$	3.63(1)	3.7
$C(1) \cdots C(19'')$	3.75(4)	3.7
$C(12) \cdots Br(6')$	4.02(1)	3.65

(*b*) Separation of chains of molecule (II) in the hexagonal layer

$C(16'^{II}) \cdots C(16'^{IV})$	3.91(2)	4.0
$C(16'^{III}) \cdots C(16'^{IV})$	4.07(2)	4.0

(*c*) Separation of chains adjacent to disordered groups

$Br(2'^{V}) \cdots Br(2'^{IV})$	3.478(3)	3.9
$C(10) \cdots C(10^{VI})$	3.89(3)	4.0

Roman numeral superscripts denote equivalent positions relative to the reference molecules at *x*, *y*, *z*:

I $x, 1 + y, z$	IV $x, y - 1, z$
II $-x, 1 - y, 1 - z$	V $-x, -y, -z$
III $-x, -y, 1 - z$	VI $1 - x, -y, -z$

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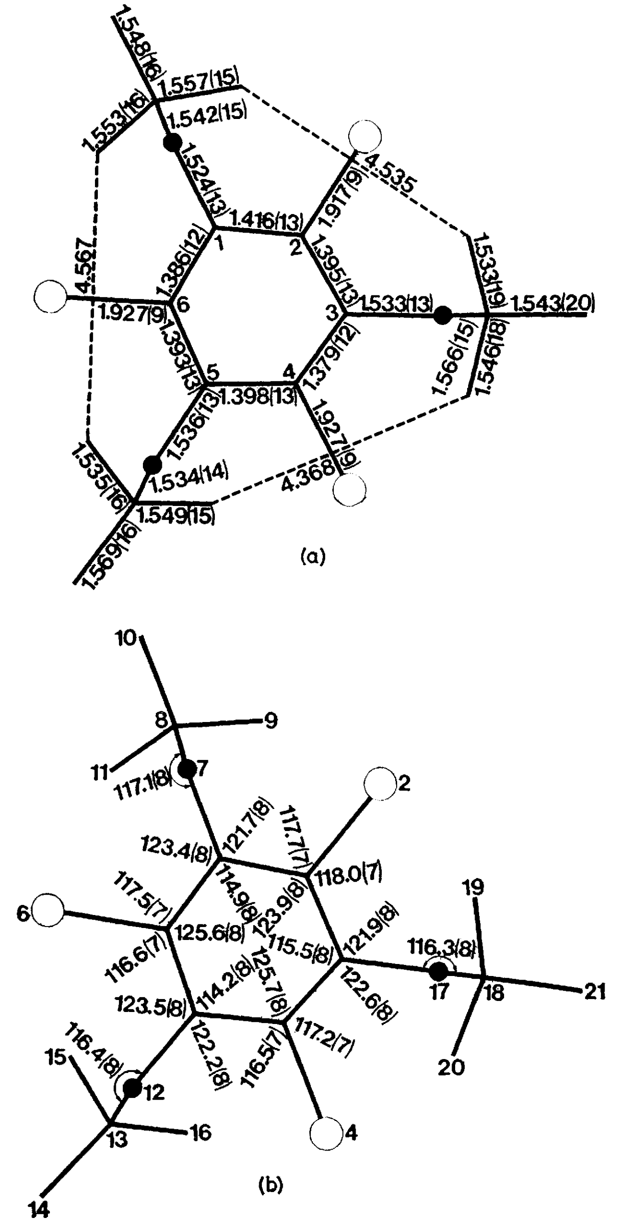
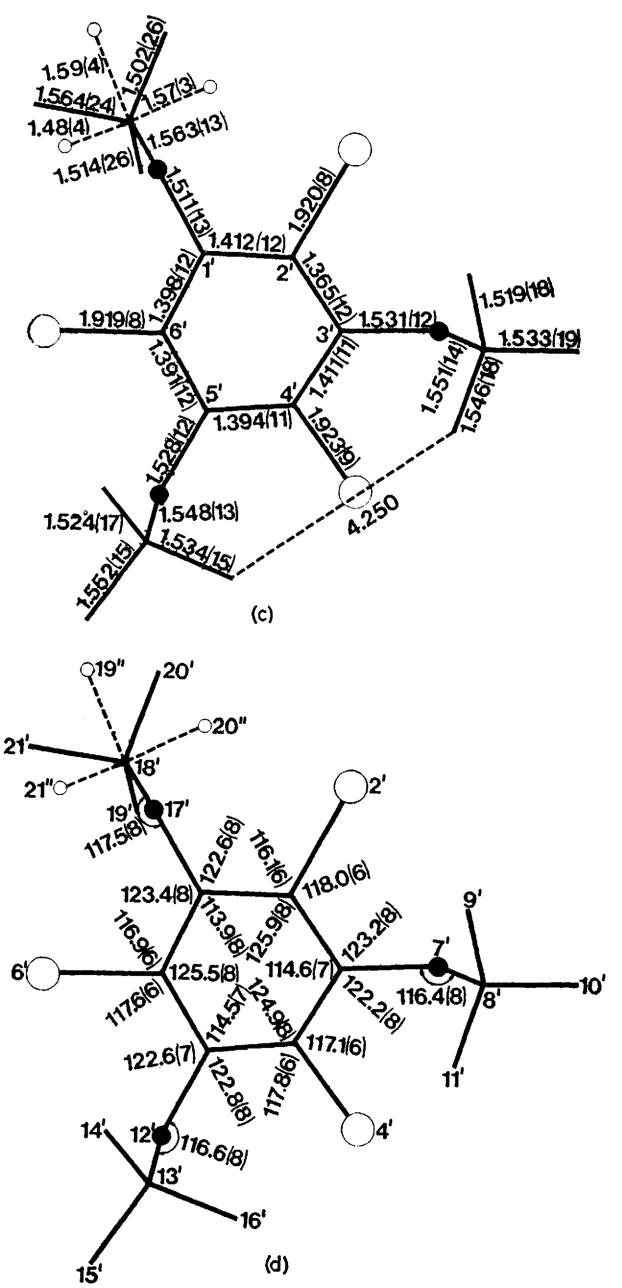
* See Notice to Authors No. 7 in *J.C.S. Perkin II*, 1977, Index issue.

as will be discussed, some indications for the operation of attractive steric effects may be gleaned from a perusal of the crystallographic data.

The unique neopentyl group of molecule (II) is disordered so that the methyl groups have two preferred orientations. The orientation calculated to occur (statistically) for 60% of the unit cells constituting the single crystal used is indicated by full lines in Figure 1 (c, d). Surprisingly, this preferred orientation is not far from that which would lead to eclipsing at the methylene group. However (see discussion of molecular packing), one of the methyl groups indicated by the full lines in Figure 1 (c, d) is in close contact [3.92(3) Å]* with a methyl group in an adjacent molecule [of type (I)]. Perhaps the preferred orientation is, on balance, the result of an attractive steric effect between C(10) and C(19′) (see Figures 1 and 3). The fact that the remaining two neopentyl groups in molecule (II) and all three of these groups in molecule (I) show essentially no evidence of a similar disorder may be at least partially interpreted in terms of attractive forces which ‘ fix ’ the relative orientations of the methyl groups. Nonetheless, the avoidance of eclipsing at the methylene group is no doubt of more importance energetically.

The numbering of the atoms and selected intramolecular distances and angles, with their estimated





FIGURES 1 Molecules (I) and (II) projected on their respective best planes showing the atom numbering system used. (a) Selected interatomic distances and (b) angles in molecules (I); (c) distances and (d) angles in molecule (II). The carbon atoms next to the benzene rings are indicated by filled circles

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* The distance as given is no doubt somewhat too short since the occupation number for C(19′) [Figures 1(d) and 3] is <1.0. (The sum of the van der Waals radii [9] is 4.0 Å in this case.)

standard deviations, are summarised for molecules (I) and (II) in Figure 1.

Torsion angles have been calculated for molecules (I) and (II), and do not deviate significantly from expected values.

Intramolecular Distances and Angles.—The carbon atoms of the $C_6Br_3C_3$ moieties [benzene ring and immediately attached C atoms (filled circles in Figure 1)] lie in a plane for both molecules, the greatest deviation of any atom from the respective best plane being 0.03 Å. All the Br atoms in molecule (I) deviate *ca.* 0.3 Å from the best plane in a direction opposite to that of the CMe_3 groups, whereas the only noteworthy deviation from the best plane of molecule (II) occurs for Br(4′) (0.5 Å), in a direction opposite to the nearest CMe_3 groups. The benzene rings are, however, somewhat deformed, probably because of the bromine substituents. Changes similar to those found here in X–C and C–C distances, and in C–C–C angles in benzene rings have been observed in a number of cases, especially for the more electronegative X atoms, F and Cl (see *e.g.* refs. 4, 5 and the survey given in ref. 6). The distortions of the benzene ring are rationalized [6] either in terms of hybridization changes or valence-shell electron-pair repulsions. In molecule (I), the angles C(1)–C(2)–C(3) 123.9(8), C(3)–C(4)–C(5) 125.7(8), and C(5)–C(6)–C(1) 125.6(8)° are significantly more acute than C(6)–C(1)–C(2) 114.9(8), C(2)–C(3)–C(4) 115.5(8), and C(4)–C(5)–C(6) 114.2(8)°.

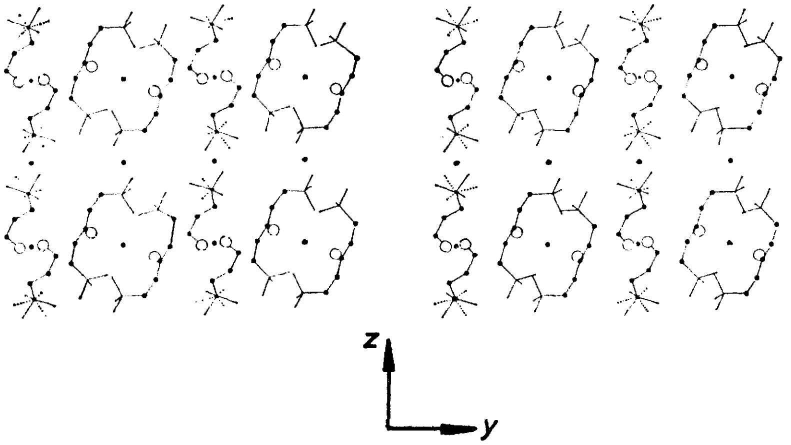

FIGURE 2 A stereoview of part of the crystal structure projected on the *YZ* plane. A right-handed co-ordinate system is used throughout in the Figures. An asterisk denotes the crystallographic origin used in Table 1

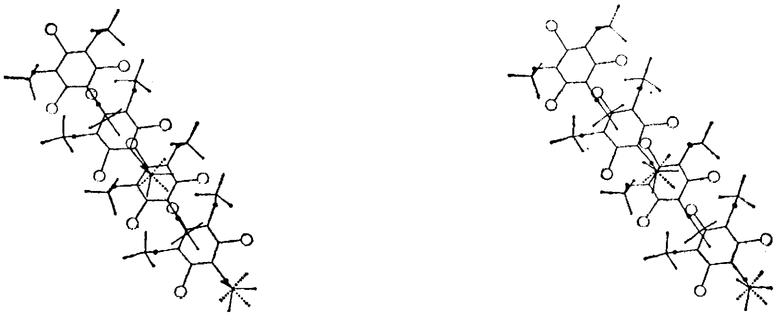

FIGURE 3 A stereoview of one row of molecules (I) and (II) extending along the *Y* axis and viewed in a direction perpendicular to the mutual best plane for molecules (I) and (II)

The Br(2)–C(2), Br(4)–C(4), and Br(6)–C(6) distances are 1.917(9), 1.927(9), and 1.927(9) Å, whereas the expected aromatic Br–C distance is 1.85(1) Å.[7] This lengthening of the Br–C bond and the deviations of the bromine atoms from the best plane (see earlier) reflect the repulsion between the bromine atoms and the carbon atoms of the neopentyl groups. The situation is similar in molecule (II) [*cf.* Figure 1 (c, d)]. Observed nonbonded distances between the methyl carbons and the appropriate nearest bromine atom are all 3.4—3.5 Å, which is significantly less than the sum of the van der Waals radii [3] (3.95 Å), and thus on the repulsive branch of the C · · · Br nonbonded potential function.

Other intramolecular nonbonded distances of interest are those between proximate methyl groups on the same side of the benzene ring, *e.g.* C(9) · · · C(19), C(11) · · · C(15), *etc.* These distances [Figure 1 (a, c)] are found,

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[4] A. Meresse, C. Courseille, F. Leroy, and N. B. Canh, *Acta Cryst.*, 1975, **B31**, 1236.

[5] B. Pedersen, *Acta Cryst.*, 1975, **B31**, 2932.

[6] A. Domenicano, A. Vaciga, and C. Coulson, *Acta Cryst.*, 1975, **B31**, 221.

[7] ' International Tables for *X*-Ray Crystallography,' Kynoch Press, Birmingham, 1962, vol. III, p. 275.

as expected, to be somewhat greater than the sum of the van der Waals radii (4.0 Å),[3] and thus capable of contributing to a lowering of the conformational energy *via* attractive steric interactions. Two of these distances in molecule (I) are 4.54 and 4.57 Å, while the third is 4.37 Å; in molecule (II) only one such interaction remains, and the corresponding nonbonded Me • • • Me distance is reduced to 4.25 Å [Figure 1(c)]. There are apparently no intermolecular interactions (revealed by short distances) which could account for this reduction, and we are consequently tempted to view it as another piece of evidence for the operation of an attractive steric effect.

Packing of the Molecules.—The best planes of the benzene rings and their nearest substituents for molecules (I) and (II) are approximately parallel. As the space group is $P\bar{1}$, all the benzene rings of the crystal structure are also parallel. The packing of the molecules is illustrated in Figures 2 and 3. All co-ordinates were first transformed to an orthogonal system with its X axis parallel to the a direction and its Z axis parallel to the c^* direction in the direct and reciprocal unit cell, respectively. Figure 2 shows a stereo-projection along the X axis of part of the crystal structure, and shows that rows of alternating molecules (I) and (II) extend along the Y axis. One such row is here, somewhat arbitrarily, chosen as the primary building block of the crystal structure.

The structure contains a number of intermolecular contacts close to the respective sums of the van der Waals radii (see Table 2). The contacts within one row parallel to the Y axis are shown at the top of Table 2. The contact C(10) • • • C(19′), referred to earlier as the possible result of an attractive steric effect, is notable since it occurs between two methyl groups and joins molecules (I) and (II) in formal pairs (*cf.* Figure 3 and footnote on p. 1035). Figure 2 shows that each row has two types of contact to other rows in planes perpendicular to the Z axis. In one of them, $-CMe_3$ groups from different rows meet and together form an infinite near-planar and approximately hexagonal layer in which two types of short contact occur (see Table 2). The short distances are, however, all quite close to the sum of the van der Waals radii, and thus less pronounced than, for example, the Me • • • Me distance of 3.62 Å observed in the crystal structures of n-octane and n-hexane.[8]

The other plane perpendicular to the Z axis (see Figure 2) is adjacent to the disordered CMe_3 groups of type (II) molecules. Two types of short contact also occur here (Table 2). These contacts result from two Br(2′) and two C(10) atoms (methyl groups), each related by a centre of symmetry.

There are no short contacts between atoms belonging to different chains above or below each other in the X direction.

The presence of equal amounts of two different rotamers in Br_3TNB in the solid state has provided us with a direct comparison of the structures of these two conformations, from which indications of the operation of intra- and inter-molecular attractive steric effects between methyl groups have been extracted. Such effects are of course quite well known, at least in principle, especially as they manifest themselves in *e.g.* the determination of vapour pressures of hydrocarbons, but the trineopentylbenzene system is an unusually fertile source of unambiguous experimental demonstrations of their existence, both in the establishment of conformational preferences in solution,[1] and now in molecular packing in the crystal.

[7/1882 *Received, 27th October,* 1977]

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[8] N. Norman and H. Mathisen, *Acta Chem. Scand.*, 1961, **15**, 1747, 1755.