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The Crystal and Molecular Structures of Tetraphenylhydrazine and Related Compounds at −160°C. III. Discussion of the Conformation of the Molecules

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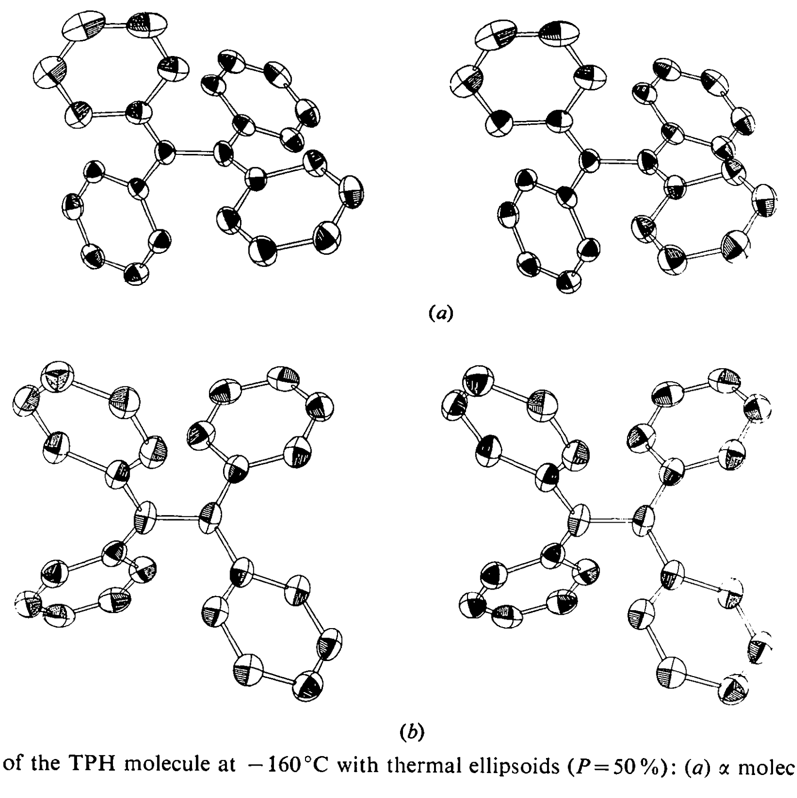
A discussion is given of the conformations of the molecules of tetraphenylhydrazine (TPH), tetraphenylethylene (TPE), diphenylaminotriphenylmethane (DTM) and *N*-(diphenylmethylene)aniline (triphenylimine, TPI). For TPH, TPE and DTM the values of the angles around the atoms of the central bonds can be explained qualitatively by considering the repulsion between non-bonded atoms. For TPI the repulsion between the lone pair of electrons at N and its neighbouring bonds also has to be taken into account. There is considerable strain in the molecules; many distances between atoms of neighbouring phenyl groups are shorter than the relevant van der Waals distances. This is partly due to the influence of π-electron delocalization which tends to keep the molecules planar. Owing to the strain in the molecules the C–C(Ph) and N–C(Ph) bonds are longer than expected. The angles of twist around the approximately double bonds in TPE (1·356 Å) and in TPI (1·286 Å) are small, 8·4 and 7·6° respectively. For the approximately single N–N bond in TPH (1·406 Å) the angle of twist is 74·1°.

Introduction

In papers I and II of this series (Hoekstra, Vos, Braun & Hornstra, 1975; Hoekstra & Vos, 1975) the determination of the crystal structures of and the packing in tetraphenylhydrazine (TPH), tetraphenylethylene (TPE) and diphenylaminotriphenylmethane (DTM) have been described. In the present paper the conformation of the molecules will be discussed and compared with the conformation of *N*-(diphenylmethylene)-aniline (triphenylimine, TPI; Tucker, Hoekstra, ten Cate & Vos, 1975).


(*a*)

(*b*)

Fig. 1. Stereo view of the TPH molecule at −160°C with thermal ellipsoids ($P=50\%$): (*a*) α molecule; (*b*) β molecule.

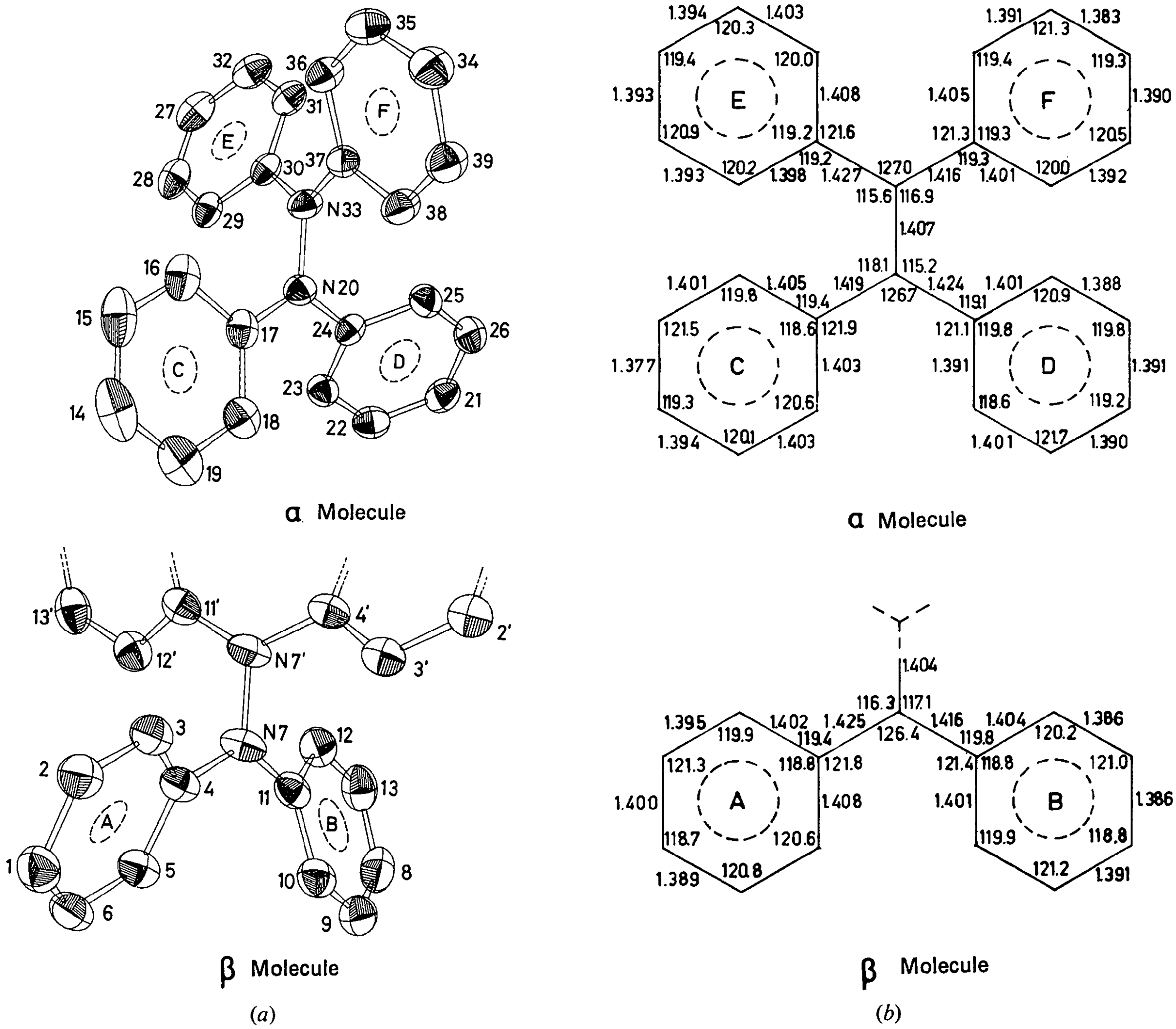
Description of the molecules

The conformation of the molecules and the numbering of the atoms are shown in Figs. 1 and 2 for TPH, in Fig. 3 for TPE and in Fig. 4 for DTM. Data concerning the (approximately) planar parts in the molecules and short intramolecular distances are listed in Table 1 for TPH, in Table 2 for TPE and in Table 3 for DTM. In Fig. 5 the numerical data of the TPI molecule, which are of interest for the present discussion, are given. Table 4 shows some characteristic features of the molecules.

Discussion

The large number of short non-bonded intramolecular distances in Tables 1 to 3 indicates that repulsion plays an important role in the molecules. Nevertheless there are many short distances between the atoms of neighbouring phenyl rings which could be lengthened by increasing the torsion angle φ of the phenyl groups. That this does not occur suggests that the molecules tend to be planar, presumably because of the influence of π-electron delocalization. In the discussion of the valence angles and of some of the bond lengths the repulsion between non-bonded atoms will be emphasized (Bartell, 1968). The phenyl groups will be considered as rigid bodies with the observed geometry.

The molecules of TPE show deviations from symmetry 222 expected for the molecules in the gas phase, and the α molecules of TPH show deviations from an 'idealized form' (paper I). No further discussion of these deviations, which we ascribe to intermolecular interactions, will be given.



α Molecule (a) α Molecule (b)

β Molecule (a) β Molecule (b)

(a) (b)

Fig. 2. Bond lengths (Å) and angles (°) in the TPH molecules at −160°C with the numbering scheme used. Standard deviations in bond lengths and angles not involving hydrogen atoms are 0·004 Å and 0·27° respectively.

The angles in the groups X–Y$<^{\mathrm{C}}_{\mathrm{C'}}$

In each of the molecules under consideration the groups X–Y(C,C′), where Y is N or tertiary C and X is N or C, are approximately planar. For TPE and TPI this is not surprising, as the bond X–Y is a double bond in these molecules. For the N–N(Ph)$_2$ groups in TPH and the C–N(Ph)$_2$ group in DTM the reasons for a planar structure around the N atom are not so obvious. It implies that in TPH and in DTM the angles around the N atoms are considerably larger than in NH_3 (H–N–H=107·3°) and in NH_2CH_3 (H–N–H=105·9 C–N–H=112·1°). According to Gillespie (1972, p. 108) the small angles in the latter compounds are caused by repulsion between the lone pairs of electrons on N and the N–H (or N–C) bonds. In TPH and in DTM this repulsion is smaller because of the delocalization of the lone pairs of electrons (Gillespie, 1972, p. 110). Moreover, small angles C–N–C or N–N–C are sterically less favourable than small angles H–N–H. It is therefore plausible that the angles around the N atoms in TPH and in DTM are relatively large.

In each of the molecules the values of the angles α and β (see Table 4) around the central atom Y are largely determined by repulsion between non-bonded atoms. In TPE where X and Y are C and X–Y is C=C the angles β are larger than the angles α (Table 4). This is because the length of a double bond is smaller than that of a single bond. The values of the bond lengths and angles are such that in the triangles around the atoms Y the C...C distances are approximately (within 0·04 Å) equal.

In TPH, where X and Y are N and X–Y is N–N, the angles β are smaller than the angles α (Table 4) in contradistinction to TPE. For TPH in the triangles around the atoms Y the shortening of C...C and C...N relative to the van der Waals distances of 3·4 and 3·2 Å respectively should be considered. In the observed structure this shortening varies from 0·78 to 0·81 Å for C···N and from 0·85 to 0·86 Å for C···C.

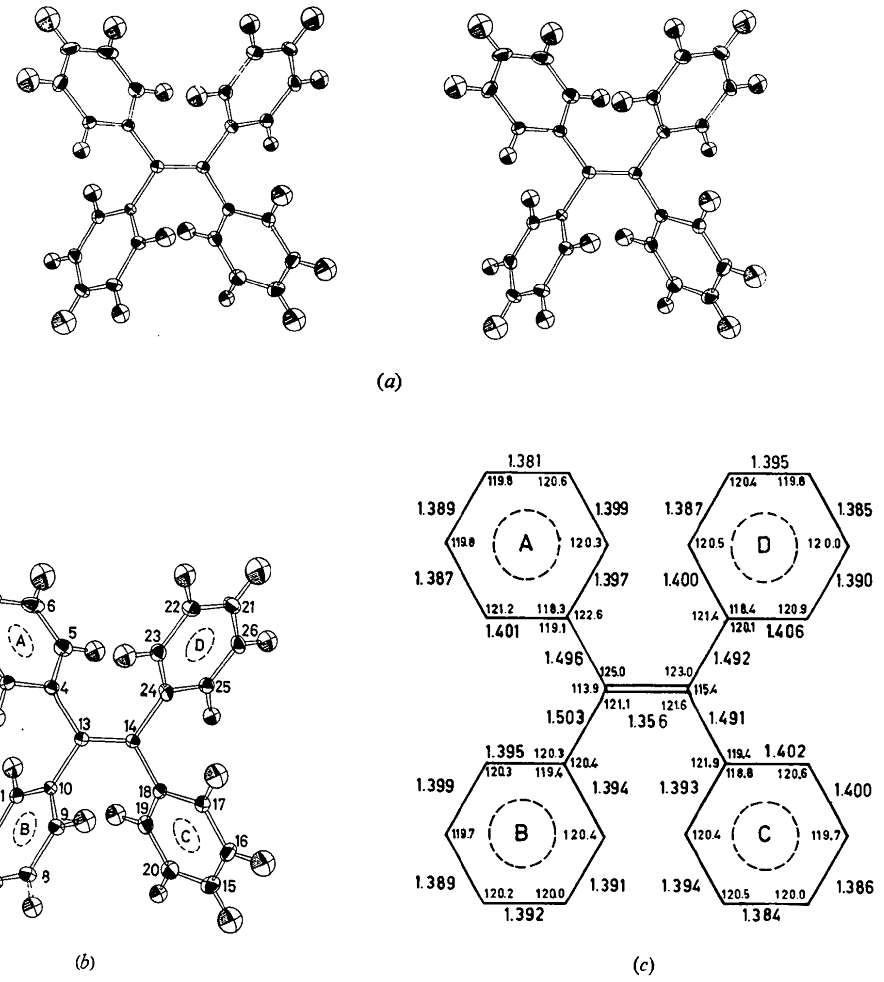


Fig. 3. Conformation of the TPE molecule at −160°C. (*a*) Stereo view of the molecule with thermal ellipsoids ($P=50\%$). (*b*) Numbering scheme used. (*c*) Bond lengths (Å) and angles (°), σ(C–C)=0·003 Å, σ(C–C–C)=0·25°.

It cannot be excluded that (part of) this difference is due to a slight underestimate of the van der Waals radius of N (1·5 Å) relative to that of C (1·7 Å). The relatively small shortening of N···C may also be ascribed, however, to repulsions between the atoms X and the phenyl groups linked to Y. That in TPH this type of repulsion is larger than in TPE can, for instance, be seen by comparing the shortening of distances of type N(20)···C(29) in TPH (0·41 Å on average) with that of distances of type C(13)···C(19) in TPE (maximum shortening 0·32 Å).

In DTM the central N atom (Y) is surrounded by three C atoms, X=C(31), C=C(19) and C′=C(25) [Fig. 4(b)]. From the fact that the bonds Y–C and Y–C′ are approximately 0·08 Å shorter than the bond Y–X, one would expect the angle α to be larger than the angles β. From Fig. 4(c) we see, however, that α is considerably (5·5°) smaller than the average value of the angles β. This is due to the relatively strong repulsion between the $N(Ph)_2$ and the $C(Ph)_3$ group in the molecule. As a result the distance C···C′=C(19)···C(25) in the triangle around Y is 0·13 Å shorter than the distances X···C and X···C′. The distortions in the $C(Ph)_3$ group due to the strain in the molecule (Hoekstra, 1974) will not be discussed in the present paper.

For TPI where Y is C, X is N and X–Y is N=C, the

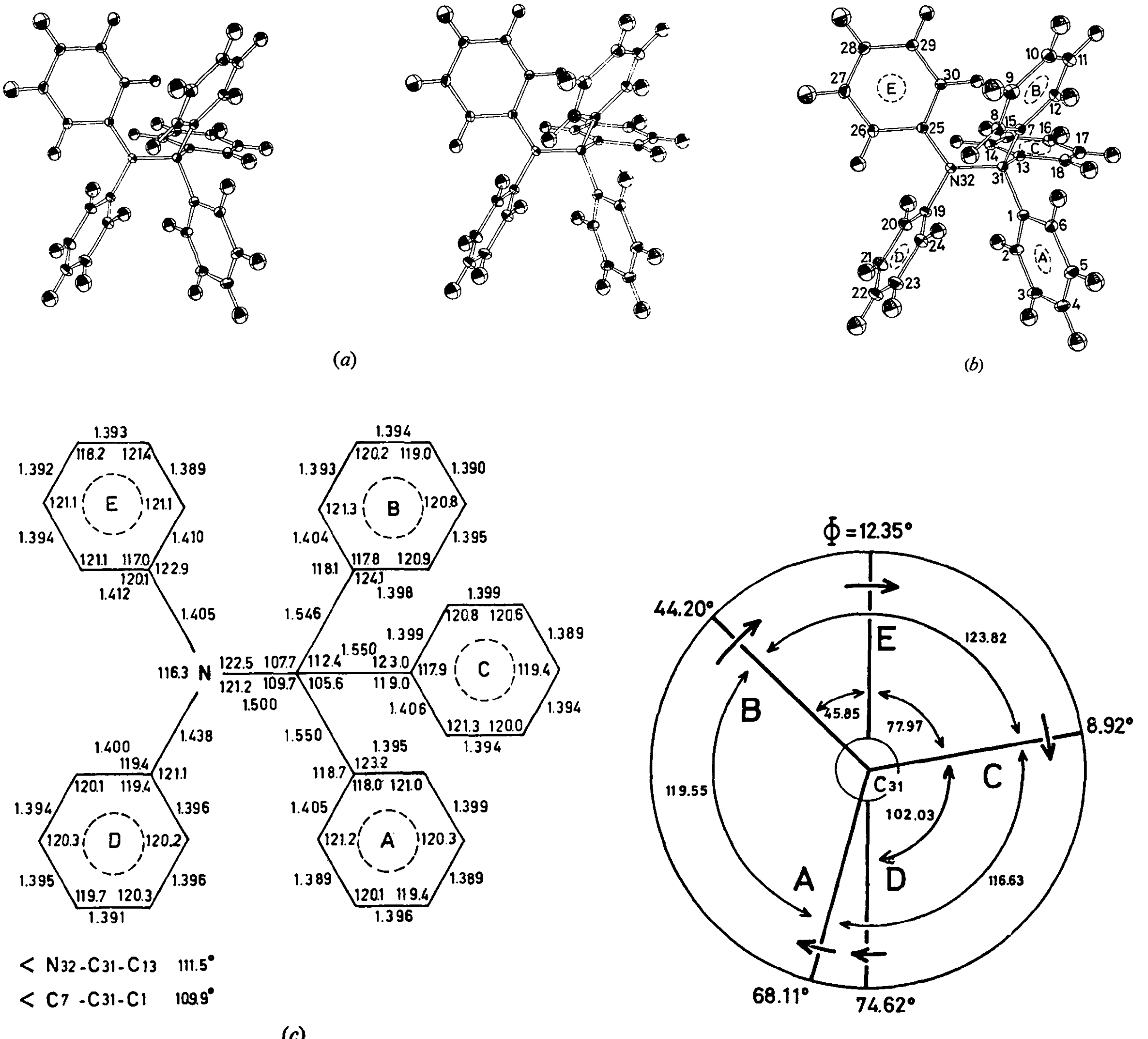


Fig. 4. Conformation of the DTM molecule at −160°C. (*a*) Stereo view of the molecule with thermal ellipsoids ($P = 50\%$). (*b*) Numbering scheme used. (*c*) Bond lengths (Å) and angles (°); standard deviations in bond lengths and angles not involving hydrogen atoms are 0·001 Å and 0·09° respectively. (*d*) Newman projection along the central C–N bond with values of the dihedral angles. Looking from the centre of the figure all phenyl groups are rotated in the same direction (see arrows) from the orientation with $\varphi = 0°$ (phenyl group parallel to central C–N bond).

angle β_1 is large in comparison with the angle β_2 (Fig. 5). The bending of β_1, which amounts to 4° in comparison with the average value of β_1 and β_2, is due to the repulsion between the phenyl groups *B* and *C*. In TPI this repulsion is expected to be stronger than the corresponding repulsion in TPE because (*a*) the central C=N bond in TPI is 0·07 Å shorter than the C=C bond in TPE; (*b*) the angle C=N–C(3) is expected

Table 1. *Numerical data for the TPH molecule at* −160°C.

For numbering of the atoms see Fig. 2.

I. Equations of the planes *A*, *B*, *C etc.* The atoms concerned are given in brackets; the equations refer to axes *X*, *Y*, *Z* parallel to **a***, **b** and **c**.
II. Deviations (in 10^{-3} Å) of the atoms from the respective planes.
III. Dihedral angles (°), φ = torsion angle of phenyl ring, θ = twist angle around central bond.
IV. Distances shorter than the sum of the relevant van der Waals radii* with differences given in parentheses. Distances of the atoms linked to the same atom are indicated by †.

I.

A [C(1) to C(6)]	$-0{\cdot}6104X+0{\cdot}7312Y-0{\cdot}3046Z=$	1·2125 Å
B [C(8) to C(13)]	$0{\cdot}6042X-0{\cdot}1765Y+0{\cdot}7770Z=$	−0·7657
C [C(14) to C(19)]	$-0{\cdot}5336X+0{\cdot}7891Y-0{\cdot}3044Z=$	−5·9159
D [C(21) to C(26)]	$-0{\cdot}0374X-0{\cdot}5587Y+0{\cdot}8285Z=$	1·4873
E [C(27) to C(32)]	$0{\cdot}7368X+0{\cdot}5458Y+0{\cdot}3990Z=$	10·7672
F [C(34) to C(39)]	$0{\cdot}1449X+0{\cdot}5675Y+0{\cdot}8105Z=$	4·4813
G [C(4), N(7), N(7′), C(11)]	$0{\cdot}7984X-0{\cdot}3728Y+0{\cdot}4729Z=$	−1·2204
H [C(17), N(20), N(33), C(24)]	$-0{\cdot}3867X+0{\cdot}8477Y-0{\cdot}3630Z=$	−4·3976
I [C(30), N(33), N(20), C(37)]	$0{\cdot}3413X+0{\cdot}7300Y+0{\cdot}5921Z=$	6·6385
J [C(4′), N(7′), N(7), C(11′)]	$0{\cdot}7984X+0{\cdot}3728Y-0{\cdot}4729Z=$	1·2202

II.

A:	C(1)	10;	C(2)	−5;	C(3)	−7;	C(4)	14;	C(5)	−9;	C(6)	−3;	N(7)	17
B:	C(8)	21;	C(9)	0;	C(10)	−23;	C(11)	25;	C(12)	−4;	C(13)	−19;	N(7)	55
C:	C(14)	0;	C(15)	−3;	C(16)	0;	C(17)	6;	C(18)	10;	C(19)	7;	N(20)	−26
D:	C(21)	10;	C(22)	2;	C(23)	−14;	C(24)	13;	C(25)	−1;	C(26)	−11;	N(20)	−2
E:	C(27)	8;	C(28)	−5;	C(29)	−7;	C(30)	16;	C(31)	−13;	C(32)	1;	N(33)	2
F:	C(34)	−17;	C(35)	6;	C(36)	13;	C(37)	−21;	C(38)	10;	C(39)	9;	N(33)	−34
G:	C(4)	9;	N(7)	−26;	N(7′)	8;	C(11)	9						
H:	C(17)	2;	N(20)	−5;	N(33)	2;	C(24)	2						
I:	C(30)	14;	N(33)	−40;	N(20)	12;	C(37)	14						

III.

φ	(*AG*)	25·32	θ	(*GJ*)	74·04	(*BB′*)	74·35
φ	(*BG*)	23·71	θ	(*HI*)	74·22	(*CF*)	82·89
φ	(*CH*)	9·68		(*AB*)	42·73	(*DE*)	89·89
φ	(*DH*)	40·54		(*CD*)	47·69	(*AB′*)	89·82
φ	(*EI*)	27·60		(*EF*)	42·27	(*CE*)	85·19
φ	(*FI*)	19·32		(*AA′*)	75·24	(*DF*)	69·57

IV.

α TPH molecule

C(17)···C(24)	2·541 (0·86)†	N(33)···C(24)	2·390 (0·81)†	C(31)···H(C36)	2·508 (0·39)
C(30)···C(37)	2·545 (0·85)†	N(20)···C(30)	2·399 (0·80)†	C(23)···H(C18)	2·529 (0·37)
C(18)···C(24)	3·022 (0·38)	N(20)···C(37)	2·406 (0·79)†	C(36)···H(C31)	2·610 (0·29)
C(30)···C(36)	3·024 (0·38)	N(33)···C(17)	2·424 (0·78)†	C(37)···H(C16)	2·653 (0·25)
C(31)···C(36)	3·070 (0·33)	N(20)···C(29)	2·761 (0·44)	C(24)···H(C18)	2·709 (0·19)
C(24)···C(30)	3·082 (0·32)	N(20)···C(38)	2·778 (0·42)	C(17)···H(C29)	2·719 (0·18)
C(17)···C(37)	3·085 (0·31)	N(33)···C(16)	2·778 (0·42)	C(18)···H(C23)	2·722 (0·18)
C(31)···C(37)	3·093 (0·31)	N(33)···C(25)	2·834 (0·37)	C(38)···H(C25)	2·723 (0·18)
C(17)···C(23)	3·103 (0·30)			C(30)···H(C36)	2·727 (0·17)
C(18)···C(23)	3·112 (0·29)	N(33)···H(C16)	2·418 (0·28)		
C(16)···C(37)	3·139 (0·26)	N(20)···H(C29)	2·423 (0·28)	H(C31)···H(C36)	2·194 (0·21)
		N(20)···H(C38)	2·440 (0·26)	H(C18)···H(C23)	2·286 (0·11)
		N(33)···H(C25)	2·579 (0·12)		

β TPH molecule

C(4)····C(11)	2·537 (0·86)†	N(7′)···C(4)	2·404 (0·80)†	C(10)···H(C5)	2·546 (0·36)
C(4)····C(10)	3·046 (0·35)	N(7′)···C(11)	2·406 (0·79)†	C(5)····H(C10)	2·589 (0·31)
C(5)····C(11)	3·046 (0·35)	N(7′)···C(12)	2·789 (0·41)	C(11)···H(C5)	2·764 (0·14)
C(5)····C(10)	3·061 (0·34)	N(7′)···C(3)	2·795 (0·40)		
C(4)····C(11′)	3·086 (0·31)			H(43–5)···H(47–10)	2·248 (0·15)
		N(7′)···H(C12)	2·454 (0·25)		
		N(7′)···H(C3)	2·480 (0·22)		

* The van der Waals radii used in the present paper are $r(\mathrm{H})=1{\cdot}2$, $r(\mathrm{C})=1{\cdot}7$ and $r(\mathrm{N})=1{\cdot}5$ Å (Pauling, 1960).

to be smaller than 120° (*viz.* 115·7°; Singh, 1965) because of the repulsion of the lone pair of electrons at the N atom; (*c*) the angles C(1,2)–C=N in TPI have a tendency to be smaller than the angles C–C=C in TPE as C···N may become approximately 0·2 Å shorter than C···C. To obtain acceptable values for the distances between the atoms of rings *B* and *C*, for instance for C(2)···C(3), the angle β_1 is bent by 4° (see above) and the angle C=N–C(3) by 5° (in comparison with Singh's value). In spite of the bending of these angles, C(2)···C(3) in TPI is still 0·04 Å shorter than the corresponding distances in TPE. For further details of the molecule, see Tucker *et al.* (1975).

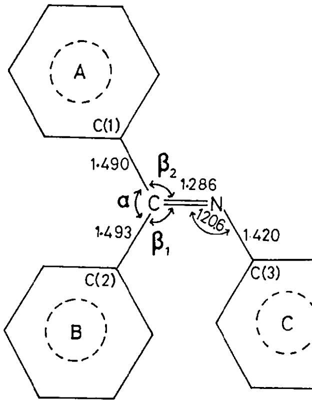


Fig. 5. Schematic drawing of the TPI molecule (Tucker *et al.*, 1975). The standard deviations in the bond lengths and angles are 0·003 Å and 0·3° respectively. $\alpha=117{\cdot}1$, $\beta_1=125{\cdot}5$, $\beta_2=117{\cdot}5$, $\varphi(A)=29{\cdot}3$, $\varphi(B)=48{\cdot}3$, $\varphi(C)=63{\cdot}4$, $\theta=7{\cdot}6°$; C(1)···C(2) = 2·544, C(2)···C(3) = 2·880 Å. The group [C(1),C(2),C,N] is approximately planar (within 0·03 Å).

Angles of twist in TPE, TPI and TPH

As we have seen above the molecules exhibit a considerable strain. Because of this there is a slight torsion around the central C=C bond in TPE (8·4°) and around the C=N bond in TPI (7·6°). The N–N bond in TPH is essentially single (PPP calculations give a π bond order of 0·03). The twist around the N–N bond in TPH reduces both the repulsions between the non-bonded atoms of the two $N(Ph)_2$ groups and the repulsion between the (partly delocalized) lone pairs on the N atoms as much as possible. For the latter repulsion an angle of twist of approximately 90° would be favorable (Jesaitis, 1973). Fig. 6 shows that

Table 2. *Numerical data for the TPE molecule at* −160° C

The numbering scheme used is given in Fig. 3(*b*). For section headings see heading Table 1.

I.

A[C(1) to C(6)]	$0{\cdot}4270X+0{\cdot}8705Y-0{\cdot}2449Z=2{\cdot}8945$ Å
B[C(7) to C(12)]	$0{\cdot}7687X-0{\cdot}4502Y+0{\cdot}4543Z=5{\cdot}8748$
C[C(15) to C(20)]	$0{\cdot}8084X-0{\cdot}4238Y-0{\cdot}4085Z=2{\cdot}2461$
D[C(21) to C(26)]	$0{\cdot}3360X+0{\cdot}6610Y+0{\cdot}6709Z=7{\cdot}7675$
E[C(4, 10, 13, 14, 18, 24)]	$-0{\cdot}2229X+0{\cdot}9579Y+0{\cdot}1811Z=1{\cdot}8057$
F[C(4, 13, 14, 10)]	$-0{\cdot}2035X+0{\cdot}9728Y+0{\cdot}1111Z=1{\cdot}5450$
G[C(18, 14, 13, 24)]	$-0{\cdot}2397X+0{\cdot}9382Y+0{\cdot}2495Z=2{\cdot}0391$

II.

A:	C(1)	−6;	C(2)	10;	C(3)	−7;	C(4)	1;	C(5)	2;	C(6)	0;	C(13)	−53
B:	C(7)	6;	C(8)	−6;	C(9)	−2;	C(10)	11;	C(11)	−11;	C(12)	2;	C(13)	54
C:	C(15)	−9;	C(16)	6;	C(17)	5;	C(18)	−13;	C(19)	10;	C(20)	1;	C(14)	−52
D:	C(21)	−4;	C(22)	−2;	C(23)	7;	C(24)	−7;	C(25)	1;	C(26)	5;	C(14)	55
E:	C(4)	−83;	C(10)	100;	C(13)	−13;	C(14)	−17;	C(18)	−85;	C(24)	98		
F:	C(4)	3;	C(13)	−8;	C(14)	3;	C(10)	3						
G:	C(18)	4;	C(14)	−12;	C(13)	5;	C(24)	4						

III.

φ	(*AF*)	42·89	(*EF*)	4·25	(*AC*)	85·63
φ	(*BF*)	57·05	(*EG*)	4·19	(*BD*)	74·60
φ	(*CG*)	46·10	(*AB*)	79·93	(*AD*)	56·32
φ	(*DG*)	45·01	(*CD*)	73·58	(*BC*)	51·20
θ	(*FG*)	8·44				

IV.

C(13)···C(18)	2·485 (0·91)†	C(4)····C(24)	3·032 (0·37)	C(10)···H(C3)	2·654 (0·25)
C(10)···C(14)	2·490 (0·91)†	C(4)····C(11)	3·076 (0·32)	C(10)···H(C19)	2·678 (0·22)
C(13)···C(24)	2·503 (0·90)†	C(13)···C(19)	3·084 (0·32)	C(4)····H(C23)	2·709 (0·19)
C(4)····C(10)	2·514 (0·89)†	C(13)···C(23)	3·096 (0·30)	C(24)···H(C17)	2·720 (0·18)
C(18)···C(24)	2·521 (0·88)†	C(9)····C(18)	3·103 (0·30)	C(18)···H(C25)	2·762 (0·14)
C(4)····C(14)	2·530 (0·87)†	C(9)····C(4)	3·114 (0·29)		
C(10)···C(18)	2·918 (0·48)	C(4)····C(23)	3·119 (0·28)		
C(3)····C(10)	2·933 (0·47)	C(5)····C(24)	3·149 (0·25)		
C(17)···C(24)	2·987 (0·41)	C(5)····C(14)	3·150 (0·25)		
C(18)···C(25)	2·998 (0·40)	C(5)····C(23)	3·204 (0·20)		
C(10)···C(19)	3·006 (0·39)	C(9)····C(19)	3·246 (0·15)		

a twist angle of 90° is not favourable for the repulsion between the phenyl groups, as in this case neighbouring phenyl rings marked with a star in the figure would become too close together (for the observed values of φ). The observed twist angles of 74·0 and 74·2° are such that each phenyl ring of the lower N(Ph)$_2$ group in the figure lies approximately at the van der Waals distances from both phenyl rings of the upper N(Ph)$_2$ group.

The bond lengths

The large elongations of the single C–C and C–N bonds in DTM (0·045 and 0·03 Å respectively, Table 4) can be ascribed to the strain in the molecule.

The approximately single N–N bond in TPH is shortened by 0·05 Å relative to the N–N bond in H_2N–NH_2 (Morino, Iijima & Murata, 1960). This bond shortening can be ascribed to the relatively small repulsion between the (partly delocalized) lone pairs of electrons on the N atoms (Gillespie, 1972) or to the relatively large *s* character of the N–N bond in TPH.

To obtain more insight into the lengths of the bonds with double bond character, we have carried out PPP calculations for the observed conformations of the molecules. The parameters used in the calculations and the bond-length bond-order curves have been taken from Nishimoto & Forster (1966). The non-

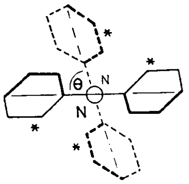


Fig. 6. Schematic drawing of the TPH molecule seen along the N–N bond. The lower N(Ph)$_2$ group is given by dashed lines. Upper parts of phenyl rings are given in heavy print. Parts indicated by * are approximately at the same height.

Table 3. *Numerical data for the DTM molecule at* −160° C

The numbering scheme used is given in Fig. 4(*b*). For section headings see heading Table 1.

I.

A[C(1) to C(6)]	0·1315*X*+0·9800*Y*−0·1493*Z*= 7·7715 Å
B[C(7) to C(12)]	−0·1766*X*−0·1027*Y*+0·9789*Z*= 0·6646
C[(13) to C(18)]	0·7682*X*+0·2345*Y*+0·5958*Z*= 5·5811
D[C(19) to C(24)]	0·1685*X*−0·6219*Y*+0·7648*Z*= −1·5228
E[C(25) to C(30)]	0·8571*X*−0·4223*Y*−0·2949*Z*= −1·4504
F[C(19), C(25), C(31), N(32)]	0·7383*X*−0·6015*Y*−0·3051*Z*= −3·0164
G[C(1), C(31), N(32)]	0·8545*X*−0·5101*Y*−0·0984*Z*= −1·4878
H[C(7), C(31), N(32)]	−0·1181*X*+0·6196*Y*+0·7760*Z*= 6·1431
I[C(13), C(31), N(32)]	−0·6948*X*−0·1495*Y*−0·7035*Z*= −4·8921

II.

A:	C(1)	−8;	C(2)	10;	C(3)	−4;	C(4)	−5;	C(5)	7;	C(6)	−1;	C(31)	30
B:	C(7)	2;	C(8)	1;	C(9)	−2;	C(10)	0;	C(11)	3;	C(12)	−4;	C(31)	50
C:	C(13)	12;	C(14)	−8;	C(15)	−2;	C(16)	9;	C(17)	−4;	C(18)	−6;	C(31)	−16
D:	C(19)	−9;	C(20)	1;	C(21)	7;	C(22)	−6;	C(23)	−2;	C(24)	10;	N(32)	24
E:	C(25)	−4;	C(26)	12;	C(27)	−9;	C(28)	−3;	C(29)	10;	C(30)	−7;	N(32)	−17
F:	C(19)	−6;	C(25)	−1;	C(31)	1;	N(32)	2						

III.

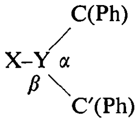
φ	(*DF*)	74·62	(*GF*)	14·60	(*CF*)	75·86	(*BC*)	64·95
φ	(*EF*)	12·35	(*HF*)	45·85	(*AB*)	74·34	(*BD*)	38·49
φ	(*AG*)	68·11	(*IF*)	77·97	(*AC*)	76·00	(*BE*)	66·63
φ	(*BH*)	44·20	(*AF*)	63·46	(*AD*)	45·46	(*CD*)	63·95
φ	(*CI*)	8·92	(*BF*)	68·45	(*AE*)	75·10	(*CE*)	67·44
							(*DE*)	79·54

IV.

C(19)···C(25)	2·415 (0·98)†	C(8)······C(25)	3·097 (0·30)	C(19)···H(C26)	2·380 (0·52)
C(1)····C(13)	2·469 (0·93)†	C(20)·····C(25)	3·120 (0·28)	C(7)····H(C30)	2·395 (0·50)
C(1)····C(7)	2·535 (0·86)†	C(12)·····C(18)	3·121 (0·28)	C(18)···H(C12)	2·397 (0·50)
C(31)···C(25)	2·548 (0·85)†	C(6)······C(8)	3·162 (0·24)	C(8)····H(C6)	2·491 (0·41)
C(31)···C(19)	2·559 (0·84)†	C(14)·····C(30)	3·195 (0·20)	C(25)···H(C14)	2·551 (0·35)
C(7)····C(13)	2·573 (0·83)†	C(1)······C(8)	3·204 (0·20)	C(13)···H(C12)	2·553 (0·35)
C(19)···C(26)	2·766 (0·63)	C(7)······C(18)	3·204 (0·20)	C(12)···H(C30)	2·557 (0·34)
C(1)····C(19)	2·797 (0·60)	C(20)·····C(26)	3·216 (0·18)	C(31)···H(C30)	2·631 (0·27)
C(2)····C(13)	2·896 (0·50)			C(13)···H(C2)	2·666 (0·23)
C(1)····C(18)	2·903 (0·50)	N(32)·····C(7)	2·460 (0·74)†	C(1)····H(C18)	2·672 (0·23)
C(7)····C(30)	2·908 (0·49)	N(32)·····C(1)	2·494 (0·71)†	C(30)···H(C14)	2·673 (0·23)
C(2)····C(19)	2·920 (0·48)	N(32)·····C(13)	2·522 (0·68)†	C(13)···H(C30)	2·694 (0·21)
C(7)····C(25)	2·929 (0·47)	N(32)·····C(8)	2·845 (0·35)	C(20)···H(C26)	2·733 (0·17)
C(12)···C(13)	2·945 (0·45)	N(32)·····C(14)	2·876 (0·32)	C(19)···H(C2)	2·735 (0·16)
C(30)···C(31)	2·990 (0·41)				
C(1)····C(24)	3·063 (0·34)	H(C8)····H(C24)	2·263 (0·14)	N(32)···H(C14)	2·478 (0·22)

Table 4. *Characteristic features observed in TPH, TPE, DTM and TPI*

Groups containing a central atom Y are indicated by



Y = N or tertiary C;
X = N or C.

Groups X–Y$<^{C}_{C'}$	Approximately planar
Torsion φ around Y–C(Ph) or Y–C′(Ph) (°)	TPH: 9·7–40·5, TPE: 42·9–57·1, DTM: 12·4 and 74·6, TPI: 29·3 and 48·3
Twist θ around X–Y (°)	TPH: 74·1, TPE: 8·4, DTM: see Fig. 4(*d*), TPI: 7·6
Average value of α (°)	TPH: 126·7, TPE: 114·6, DTM: 116·3, TPI: 117·1
Average value of β (°)	TPH: 116·5, TPE: 122·7, DTM: 121·8, TPI: 121·5
Lengths of central bonds	TPH: 0·05 Å shorter than in H_2N-NH_2.[1] TPE: 0·02 Å longer than in H_2C=CH_2.[2] DTM: 0·03 Å longer than C–N (single).[3]
Remaining angles and bonds	DTM: C–C(Ph) 0·045 Å longer than C(sp^3)–C(sp^2) single bond.[4] Angles around tetrahedral C atom: 105·6–112·4°.

References: 1. Morino, Iijima & Murata (1960). 2. Bartell & Bonham (1959). 3. Gillespie (1972), p. 18. 4. Bastiansen & Trætteberg (1962).

planarity of the molecules has been accounted for in the usual way (Murrell & Harget, 1972). For the central (approximately double) bonds in TPE and TPI the observed lengths only deviate by one standard deviation from the respective calculated values. In contradistinction to this in the four molecules considered the Y–C(Ph) bonds are slightly longer than the calculated values. The average elongations are 0·028 Å (TPH), 0·017 Å (TPE), 0·015 Å (DTM) and 0·016 Å (TPI). It is reasonable to assume that these elongations are due to the fact that in the molecules under discussion the repulsion is stronger than in the molecules from which the bond-length bond-order curves have been derived.

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