The Crystal and Molecular Structure of *N*-(Diphenylmethylene)aniline at −160°C

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N-(Diphenylmethylene)aniline, $C_{19}H_{15}N$, is orthorhombic with $a = 8\cdot436$ (3), $b = 18\cdot771$ (5), $c = 17\cdot361$ (5) Å at − 160°C, space group *Pbca*, $Z = 8$. The atomic positions have been determined by direct methods and refined by least-squares analysis of counter data measured at − 160°C. Refinement converges with an *R* of 0·088 for 5832 reflexions. Mean bond lengths are C–C (in phenyl rings) 1·393, C(sp^2)–C(phenyl) 1·492, C(sp^2)=N 1·287 and C(phenyl)–N 1·420 Å. The molecular geometry is compared with that of triphenylnitrone. The orientation of the phenyl groups and the relation between experimental bond lengths and calculated bond orders is discussed.

Introduction

In this paper we present the crystal and molecular structure of *N*-(diphenylmethylene)aniline (triphenyl-imine, TPI). The work is part of a study undertaken at this laboratory to determine the structures of molecules comprising a central C–C, C–N or N–N group with a varying number of phenyl substituents. In the near future the structure determinations of tetra-phenylhydrazine (TPH), tetraphenylethylene (TPE) and diphenylamine–triphenylmethane (DTM) at − 160°C (Hoekstra, 1974) will be published. There are two primary purposes, firstly to provide data on how the conformations of the molecules depend on the number of phenyl groups and how the conformations are influenced by changes in the central group, and secondly to see how the bond lengths are affected by steric hindrance. The structure of triphenylnitrone (TPN: Brown & Trefonas, 1973) provided data for a study of the changes in molecular geometry on replacing the lone pair on nitrogen in TPI with an oxygen atom.

Experimental

Pale-yellow rectangular crystals of TPI were grown from 96% alcohol solutions. The crystallographic data are given in Table 1. The cell dimensions were obtained, at − 160°C, from zero-layer Weissenberg photographs

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Table 1. *Crystal data*

$C_{19}H_{15}N$, triphenylimine,	$V = 2748\cdot5$ Å^3
Orthorhombic	$Z = 8$
$a = 8\cdot436$ (3) Å at − 160°C	$F(000) = 1088$
$b = 18\cdot771$ (5)	$\lambda(\text{Mo } K\alpha) = 0\cdot71069$ Å
$c = 17\cdot361$ (5)	$\mu(\text{Mo } K\alpha) = 0\cdot78$ cm^{-1}
Space group *Pbca*	

Systematic absences: $0kl$ when k is odd, $h0l$ when l is odd and $hk0$ when h is odd.

taken with Cu $K\alpha$ radiation. Sodium chloride reflexions were superimposed for calibration. There is no phase transition between − 160°C and room temperature.

The intensities were measured on a Nonius 3-circle automatic diffractometer at − 160°C. The cooling apparatus has been described by van Bolhuis (1971). 9472 reflexions with $\theta < 40°$ were measured with a $\theta/2\theta$ scan technique and Zr-filtered Mo radiation. Attenuation filters were used to avoid errors caused by non-linearity of the counting system. Of the measured reflexions 5832 were considered to have significant intensity $[3\sigma(F) \le \langle \sigma^2(F) \rangle^{1/2}]$. The intensities were corrected for Lorentz and polarization effects but not for absorption.

Structure determination and refinement

The data were placed on an absolute scale by Wilson's (1942) method and normalized structure factors, $|E_{hkl}|$, were computed for reflexions with $\theta \le 30°$. Reflexions with $30° < \theta < 40°$ were not considered in order to reduce computing time. Intensity statistics are listed in Table 2. Triple products were generated for the 781 reflexions with $|E| > 1\cdot5$. From the $\sum_2$ relationship (Karle & Karle, 1966) the phases of 441 reflexions were determined. The positions of the 20 non-hydrogen atoms were located from the resultant *E* map.

Table 2. *Distribution of normalized structure factors*

		Theoretical	
	Experimental	Centric	Acentric
$|E| > 1\cdot0$	30·1%	31·7%	36·8%
$|E| > 2\cdot0$	5·0%	4·6%	1·8%
$|E| > 3\cdot0$	0·5%	0·3%	0·01%
$\langle |E| \rangle$	0·780	0·798	0·886
$\langle |E|^2 \rangle$	0·998	1·000	1·000
$\langle |E^2 - 1| \rangle$	1·018	0·968	0·736

The least-squares refinement was carried out with the X-RAY system of crystallographic programs (1970). The function minimized was $\sum w(F_o - F_c)^2$.

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Scattering factors were taken from *International Tables for X-ray Crystallography* (1962). In the preliminary stages of refinement the data set was limited to those reflexions with $\sin \theta/\lambda \le 0.7$ Å^{-1}. Four cycles of full-matrix least-squares refinement on positional and isotropic thermal parameters reduced R to 0.123 for 3345 reflexions. At this stage hydrogen atoms, with positions calculated from the molecular geometry assuming C–H = 1.08 Å, were included with an isotropic temperature factor of $B = 1.0$ Å^2. During the subsequent refinement, shifts in the positional parameters of each hydrogen atom equal to the shifts for the carbon atom to which it is bonded were applied. On inclusion in the refinement of anisotropic thermal parameters for the non-hydrogen atoms the least-squares matrix was divided into three, one block relating to parameters associated with the atoms C(1)–C(13) and H(1)–H(13) (the atom numbering is given in Fig. 1), a second to overall scale and temperature factors and the third to the remaining parameters. In the final cycles two additional conditions were imposed: (i) A weighting scheme was introduced in order that $\langle w(F_o - F_c)^2 \rangle$ be approximately constant over the whole range of $|F_o|$. The weight was given by $w = 40.0/|F_o|$ if $|F_o| > 40.0$ and $w = 1.0$ otherwise. (ii) 185 reflexions with $|F_o| < 0.33|F_c|$ and having small values of $|F_o|$, were excluded from the refinement. Convergence was achieved after ten cycles. The maximum parameter shift in the final cycle was 0.09σ. The final R $[= \sum(|F_o| - |F_c|)/\sum|F_o|]$ is 0.088 for 5832 reflexions.* A difference synthesis calculated at the end of the refinement shows maxima on the C–C bonds with a mean value of 0.3 (1) e Å^{-3}. At places not

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30745 (47 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 3. *Fractional coordinates with estimated standard deviations* ($\times 10^5$)

|	x/a	y/b	z/c
C(1)	17419 (17)	73215 (7)	6789 (8)
C(2)	18819 (20)	71153 (8)	−878 (8)
C(3)	30490 (20)	66320 (8)	−3062 (8)
C(4)	40795 (19)	63557 (8)	2449 (8)
C(5)	39227 (17)	65514 (7)	10152 (8)
C(6)	27547 (15)	70385 (7)	12385 (7)
C(7)	25831 (17)	72386 (7)	20666 (7)
C(8)	25595 (17)	66466 (7)	26382 (7)
C(9)	31250 (19)	67628 (9)	33826 (8)
C(10)	31191 (22)	62180 (9)	39239 (9)
C(11)	25480 (23)	55472 (9)	37215 (10)
C(12)	19850 (23)	54242 (8)	29800 (10)
C(13)	19877 (21)	59714 (7)	24393 (9)
C(14)	26518 (18)	84721 (7)	18289 (8)
C(15)	41184 (19)	86106 (8)	14933 (9)
C(16)	43166 (21)	92128 (8)	10358 (9)
C(17)	30618 (22)	96784 (8)	9126 (9)
C(18)	16081 (21)	95456 (8)	12531 (9)
C(19)	13948 (20)	89469 (8)	17196 (9)
N	24504 (17)	78779 (6)	23258 (7)
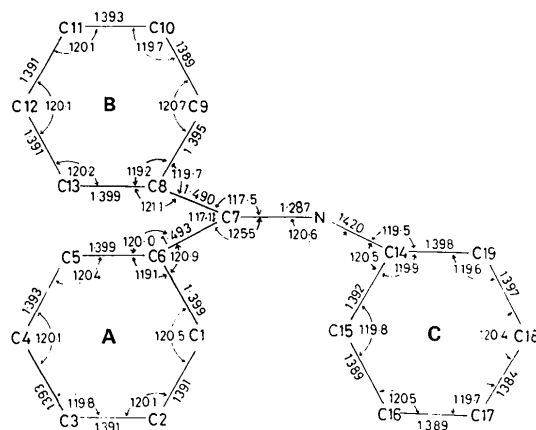
Fig. 1. Bond lengths (Å) and angles (°) in TPI.

Table 4. *Anisotropic thermal parameters* (Å$^2 \times 10^4$) *with their estimated standard deviations*

Temperature factors are in the form: $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{23}klc^*b^* + 2U_{13}hla^*c^*)]$.

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(1)	186 (5)	175 (5)	181 (5)	9 (4)	−18 (4)	1 (4)
C(2)	258 (7)	218 (6)	172 (5)	−20 (5)	−39 (5)	1 (4)
C(3)	288 (7)	208 (6)	153 (5)	−35 (5)	22 (5)	−14 (4)
C(4)	235 (6)	187 (5)	177 (5)	3 (5)	46 (5)	−17 (4)
C(5)	190 (5)	163 (5)	165 (5)	26 (4)	16 (4)	−5 (4)
C(6)	155 (5)	135 (4)	152 (4)	2 (4)	1 (4)	−1 (4)
C(7)	175 (5)	149 (5)	156 (4)	20 (4)	4 (4)	−3 (4)
C(8)	189 (5)	162 (5)	147 (5)	31 (4)	13 (4)	12 (4)
C(9)	230 (6)	253 (6)	168 (5)	10 (5)	−18 (5)	17 (5)
C(10)	276 (8)	365 (8)	198 (6)	72 (7)	−8 (6)	82 (6)
C(11)	326 (8)	257 (7)	260 (7)	120 (6)	73 (6)	108 (6)
C(12)	367 (8)	171 (6)	272 (7)	56 (6)	118 (6)	35 (5)
C(13)	308 (7)	155 (5)	195 (6)	12 (5)	62 (5)	1 (4)
C(14)	228 (6)	131 (4)	164 (5)	9 (4)	0 (4)	23 (4)
C(15)	226 (6)	175 (5)	229 (6)	2 (5)	1 (5)	−20 (5)
C(16)	286 (7)	187 (6)	249 (6)	−38 (5)	29 (6)	−20 (5)
C(17)	364 (8)	146 (5)	202 (6)	−24 (5)	18 (6)	−14 (4)
C(18)	320 (8)	157 (5)	227 (6)	46 (5)	−8 (6)	−5 (5)
C(19)	250 (6)	158 (5)	220 (6)	26 (5)	10 (5)	−18 (5)
N	246 (5)	150 (4)	175 (4)	25 (4)	11 (4)	−13 (4)

Table 5. *Fractional coordinates of the hydrogen atoms* ($\times 10^4$)

Isotropic temperature factor set with $B = 1 \cdot 0$ Å^2.

	x/a	y/b	z/c
H(1)	800	7679	854
H(2)	1051	7294	−523
H(3)	3132	6497	−912
H(4)	5088	6035	73
H(5)	4714	6331	1447
H(9)	3552	7292	3520
H(10)	3497	6323	4510
H(11)	2555	5138	4162
H(12)	1559	4900	2816
H(13)	1521	5906	1862
H(15)	5139	8274	1601
H(16)	5485	9295	791
H(17)	3210	10159	575
H(18)	645	9923	1190
H(19)	270	8833	1995

related to the molecules a few minima, none larger than $0 \cdot 4$ e Å^{-3}, are found.

The final atomic coordinates and thermal parameters are given in Tables 3–5. No satisfactory interpretation of the anisotropic thermal parameters could be obtained by treating the entire molecule as a rigid body (Pawley, 1963). The bond lengths and angles given in Fig. 1 have, therefore, not been corrected for libration effects. However the analysis does suggest an average r.m.s. value of libration of the individual phenyl groups about the respective C–C(Ph) bonds of 3°.

Discussion

Bond lengths, bond angles and the atomic numbering are shown in Fig. 1. It is generally accepted that the standard deviations derived from the least-squares treatment are underestimates. After multiplying these values by $1 \cdot 5$ no e.s.d. is greater than $0 \cdot 004$ Å for a
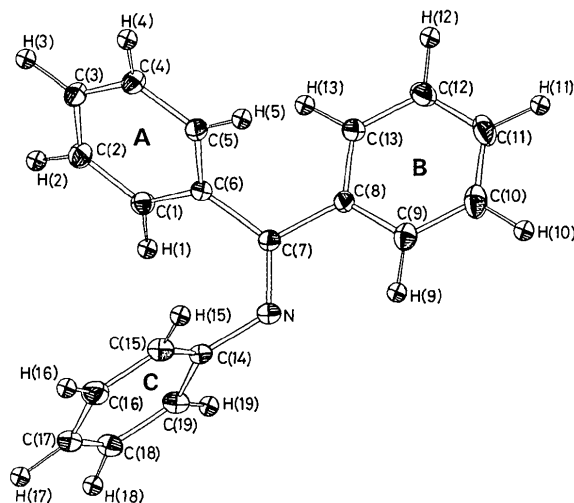

Fig. 2. Molecular geometry of TPI showing the orientation of the thermal ellipsoids.

bond length or $0 \cdot 4°$ for an angle. The mean phenyl C–C bond length of $1 \cdot 393$ (1) Å is not significantly different from its accepted value (*Tables of Interatomic Distances and Configuration in Molecules and Ions*, 1965). The molecular geometry, showing the orientation of the thermal ellipsoids, is illustrated in Fig. 2.

Phenyl group orientation

The dimensions of, and the positions of the molecules in, the cell show the structure of TPI to be approximately isomorphous with that of triphenylnitrone (TPN: Brown & Trefonas, 1973). Therefore in comparing the molecular geometry of these two compounds we shall ignore intermolecular forces. The molecule of TPI is not planar as this would make some of the non-bonded distances too short. The dihedral angles between the phenyl ring mean planes and the plane of the central skeleton are given in Table 6 where they are compared with the corresponding angles in TPN. That both molecules are strained in a similar way is apparent from the similar short non-bonded intramolecular distances, all shorter than the sum of estimated van der Waals radii for the atoms ($3 \cdot 4$ Å for C···C and $3 \cdot 2$ Å for C···N: Pauling, 1960), given in Table 7.

Table 6. *Equations of mean planes through sets of atoms and distances* (Å) *of atoms from the plane* (*in square brackets*)

Plane (*a*) Phenyl ring *A*: C(1), C(2), C(3), C(4), C(5), C(6)

$$0 \cdot 6363x + 0 \cdot 7556y - 0 \cdot 1554z = 11 \cdot 130$$

[C(1) $0 \cdot 007$; C(2) $-0 \cdot 004$; C(3) $-0 \cdot 004$; C(4) $0 \cdot 009$; C(5) $-0 \cdot 006$; C(6) $-0 \cdot 002$]

Plane (*b*) Phenyl ring *B*: C(8), C(9), C(10), C(11), C(12), C(13)

$$0 \cdot 9177x - 0 \cdot 2701y - 0 \cdot 2914z = -2 \cdot 722$$

[C(8) $-0 \cdot 001$; C(9) $0 \cdot 001$; C(10) $-0 \cdot 001$; C(11) $-0 \cdot 001$; C(12) $0 \cdot 001$; C(13) $-0 \cdot 001$]

Plane (*c*) Phenyl ring *C*: C(14), C(15), C(16), C(17), C(18), C(19)

$$0 \cdot 2790x + 0 \cdot 5247y + 0 \cdot 8043z = 11 \cdot 532$$

[C(14) $-0 \cdot 009$; C(15) $0 \cdot 003$; C(16) $0 \cdot 004$; C(17) $-0 \cdot 005$; C(18) $-0 \cdot 002$; C(19) $0 \cdot 009$]

Plane (*d*) N, C(7), C(14)

$$0 \cdot 9778x - 0 \cdot 0128y + 0 \cdot 2091z = 3 \cdot 055$$

Plane (*e*) N, C(7), C(6), C(8)

$$0 \cdot 9946x + 0 \cdot 0596y + 0 \cdot 0855z = 3 \cdot 283$$

[N $-0 \cdot 0004$; C(7) $-0 \cdot 0003$; C(6) $0 \cdot 0010$; C(8) $0 \cdot 0003$]

Dihedral angles between planes compared with equivalent angles in triphenylnitrone

Planes	TPI	TPN*
(*a*) (*e*)	$48 \cdot 3°$	$57 \cdot 9°$
(*b*) (*e*)	$29 \cdot 3$	$31 \cdot 6$
(*c*) (*d*)	$63 \cdot 4$	$67 \cdot 7$
(*e*) (*d*)	$7 \cdot 6$	$3 \cdot 4$

* Brown & Trefonas (1973).

Table 7. *Intramolecular distances* (Å)

Distance	Triphenylimine	Triphenyl-nitrone*
C(6)···C(14)	2·88	2·85
C(6)···C(13)	2·96	2·92
C(1)···N	3·10	3·11
C(1)···C(14)	3·05	3·07
C(5)···C(8)	3·05	3·09
C(5)···C(13)	3·16	3·27
C(7)···C(15)	3·05	3·14
C(6)···C(15)	3·20	3·19
C(9)···N	2·84	2·99

* Brown & Tiefonas (1973).

The two shortest C···C distances, C(6)···C(14) and C(6)···C(13) are approximately equal in both molecules. Because of the repulsion between C(6) and C(14) the geometry of the central skeleton is distorted. For TPI the angle N–C(7)–C(6), 125·5°, is enlarged in comparison with the angle N–C(7)–C(8), 117·5°. Also the angle C(7)–N–C(14) is larger than expected; it should be smaller than 120° as the repulsion of the nitrogen lone pair on neighbouring bonds is larger than the repulsion exerted by a single or double bond, and may be contrasted with the average value of more than 20 C=N–C angles in aromatic heterocyclic compounds (115·7 ± 0·2°: Singh, 1965). In TPN, where the nitrogen lone pair is replaced by an oxygen atom, the angle C=N–C, 122·4°, is larger than in TPI. The angle C(6)–C(7)–N in TPN, 119·9°, is smaller than in TPI owing to the increase in the C=N–C angle and the increase in the lengths of the C(7)–N and N–C(14) bonds (Table 8). The distance C(6)···C(13), as well as the distance C(9)···N, can be lengthened and the strain between ring *B* and its neighbouring atoms relieved by an increase in the dihedral angle between this ring (see Fig. 2) and the central skeleton. That this is not the case suggests that the molecule is attempting to remain planar, presumably to maximize delocalization of electrons. In tetraphenylethylene, $Ph_2C=CPh_2$, distances of type C(6)···C(13) range from 2·933 to 3·076 Å (Hoekstra, 1974).

The orientation of ring *A* is governed largely by the C(5)···C(8), C(1)···C(14) and C(1)···N distances. The C(1)···N and C(1)···C(14) distances are approximately the same in TPI and TPN. Because of, in

Table 8. *Bond orders and charge densities of the central skeleton of triphenylimine and triphenylnitrone*

p: Calculated bond order. r_{calc}: Calculated bond lengths from the relationship $r_{C-X} = R_{C-X} - 0·18p$ (Nishimoto & Forster, 1966) where R_{C-X} is the hypothetical sp^2-sp^2 C–X single bond length, 1·517 Å for X=C and 1·451 Å for X=N. r_{exp}: Experimental bond length. *e*: Calculated charge density.

	Triphenylimine			Triphenylnitrone		
	p	r_{calc}	r_{exp}	*p*	r_{calc}	r_{exp}
C(7)—N	0·91	1·288	1·287	0·78	1·311	1·326
C(7)—C(8)	0·27	1·469	1·490	0·31	1·461	1·464
C(7)—C(6)	0·20	1·481	1·493	0·18	1·484	1·486
C(14)–N	0·16	1·423	1·420	0·10	1·433	1·459
N——O				0·43		1·300

	e			*e*		
N	1·23			1·35		
C(19)	0·82			0·98		
O				1·71		

particular, the larger C(6)–C(7)–N angle retention of the C(1)···N distance allows the dihedral angle between the plane of ring *A* and the central skeleton to decrease in TPI relative to TPN. For C(1)···C(14) the larger average value of the angles C(6)–C(7)–N and C(7)–N–C(14) in TPI (123·0°) relative to TPN (121·1°) balances the shortening of the C(7)–N and N–C(14) bonds. The decrease of the dihedral angle of ring *A* in TPI, and the approximate compensation for the decrease of the C(8)–C(7)–C(6) angle by the lengthening of the bonds C(8)–C(7) and C(7)–C(6) (Table 8), necessitates the distances C(5)···C(8) and C(5)···C(13) to be smaller in TPI than in TPN.

The orientation of ring *C* is controlled by the interaction with ring *A*. In spite of the longer C(7)–N and N–C(14) bonds in TPN, the centres of rings *A* and *C* in TPN are nearer to each other than in TPI owing to the smaller average value for the C(6)–C(7)–N and C(7)–N–C(14) angles in TPN. A decrease in the interring distances, *e.g.* C(1)···C(15), in TPN is avoided by an increase of the torsion angle of ring *C*.

Bond lengths and bond orders

In order to have further information on π-bond orders we performed SCF–π-electron–LCAO–MO calculations on TPI and TPN with the Pariser–Parr–Pople approximation. The integrals were taken from
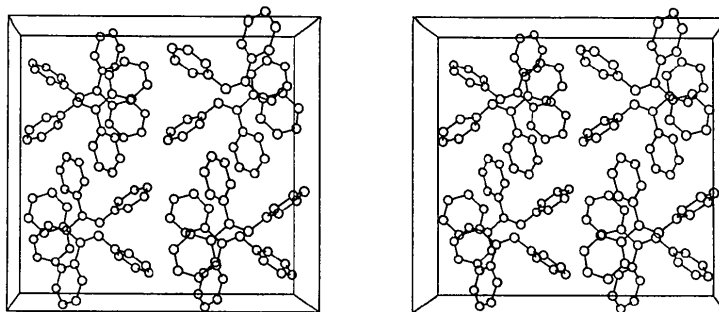

Fig. 3. Stereoscopic drawing of the unit-cell contents.

Nishimoto & Forster (1966). The σ core of the central skeleton was assumed to be $>C^+-N^+-$ for TPI and $>C^+-N^{2+}_<-O^+$ for TPN. The results are listed in Table 8. The theoretical and experimental bond lengths are equal within experimental error except for C(7)–C(8) in TPI and C(14)–N in TPN. That, on the average, the C–C(Ph) bonds are longer than the theoretical values may be a result of the van der Waals repulsions in these molecules being stronger than in the molecules from which the bond length/bond order curves have been derived.

The difference, between the two molecules, in the C(7)–N, as well as the N–C(14), length can be explained qualitatively by considering the VB resonance structures. Owing to the presence of the oxygen atom the resonance structures II(b) and II(c) contribute more to the structure of TPN than do I(b) and I(c) to TPI. The C(7)–N bond length in TPI, although shorter than that in nitrones, is similar in length to that found in oximes (*e.g.* 1·289 Å in 1,2-benzisothiazol-3-yl methyl ketoxime: Braibanti, Pellinghelli, Tiripicchio & Tiripicchio Camellini, 1973) showing that resonance structures of the type (b) and (c) are also less important in this class of compounds.
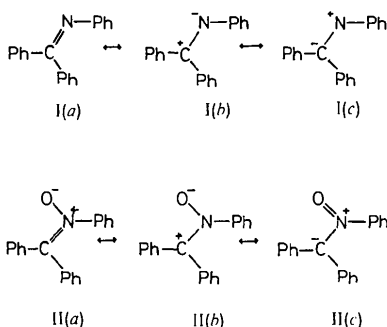
Arrangement of the molecules

The packing of the molecules in the cell is shown in Fig. 3. There are no intermolecular C···C distances shorter than 3·5 Å. There are three H···H contacts (Table 9) shorter than the van der Waals diameter of a hydrogen atom (2·4 Å: Pauling, 1960) and nine C···H

contacts (Table 9) shorter than the sum of van der Waals radii (2·9 Å: Pauling, 1960).

Table 9. *Intermolecular distances* (Å)

Code for symmetry-related atoms

Superscript	Coordinates		
None	x	y	z
i	x	$1\frac{1}{2}-y$	$-z$
ii	$1-x$	$\frac{1}{2}+y$	$\frac{1}{2}-z$
iii	$\frac{1}{2}+x$	y	$\frac{1}{2}-z$
iv	$\frac{1}{2}-x$	$-\frac{1}{2}+y$	z
v	$-x$	$\frac{1}{2}+y$	$\frac{1}{2}-z$

H(15)–H(2^i)	2·29	C(13^{iii})–H(5)	2·81
H(16)–H(11^{ii})	2·29	C(15)—H(19^{iii})	2·83
H(9)—H(1^{iii})	2·30	C(11^{iii})–H(5)	2·82
C(3)—H(1^i)	2·82	C(12^{iii})–H(5)	2·75
C(18^i)–H(4)	2·85	C(17^{iv})–H(13)	2·85
C(15)–H(2^i)	2·89	C(12^v)—H(18)	2·81

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