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The Crystal and Molecular Structures of Tetraphenylhydrazine and Related Compounds at −160°C. II. The Crystal Structures of Tetraphenylethylene (TPE) and Diphenylaminotriphenylmethane (DTM)

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The crystal structures of tetraphenylethylene (TPE) and diphenylaminotriphenylmethane (DTM) have been determined by X-ray diffraction at −160°C. TPE crystallizes in space group $P2_1$, $a=9{\cdot}798$ (2), $b=9{\cdot}175$ (2), $c=10{\cdot}781$ (2) Å, $\beta=107{\cdot}94$ (1)°, $Z=2$. The space group of DTM is $P2_1/c$, $a=8{\cdot}195$ (1), $b=17{\cdot}659$ (1), $c=16{\cdot}970$ (2) Å, $\beta=118{\cdot}08$ (1)°, $Z=4$. The intensities were measured with Zr-filtered Mo radiation on a Nonius AD-3 diffractometer. Both structures were solved by direct methods and refined by block-diagonal least-squares calculations. Anisotropic temperature factors were used for the heavy atoms. The weighted R is 0·085 for 4477 independent TPE reflexions and 0·082 for 11227 independent DTM reflexions. A discussion of the packing of the molecules in the crystal is given. Root-mean-square U_{ii} (main axes) values are in the order DTM < TPE < TPH(tetraphenylhydrazine).

Introduction

The results of the structure determination of tetraphenylhydrazine (TPH) described in paper I (Hoekstra, Vos, Braun & Hornstra, 1975) have excited our interest in the conformations of molecules consisting of a central C–C, C–N or N–N group with phenyl groups linked to it. In other papers a discussion has been given of the crystal and molecular structures of *trans*-stilbene (TSB; Hoekstra, Meertens & Vos, 1975) and *N*-(diphenylmethylene)aniline (triphenylimine, TPI. Tucker, Hoekstra, ten Cate & Vos, 1975). The present paper deals with the determination of the structures of tetraphenylethylene (TPE) and diphenylaminotriphenylmethane (DTM) by X-ray diffraction at −160°C, and with the packing of the molecules in the crystals. In paper III of this series (Hoekstra & Vos, 1975) the molecular conformations of TPE, DTM and TPH will be discussed and compared with the conformation of TPI.

Experimental

A sample of TPE was kindly provided by Dr L. Jonkman; the compound DTM was prepared according to the method of Baum, Lehn & Tamborski (1964) by Drs J. Geusendam (Laboratory of Physical Chemistry of this University). Crystals of TPE were obtained from a solution in toluene by slow evaporation. Crystals of DTM were grown by cooling a solution in benzene. The crystallographic data are given in Table 1.

Weissenberg photographs of different layer lines were used to determine the space groups. The cell dimensions were obtained from zero layer line Weissenberg films by the method described in paper I. For this purpose TPE and DTM crystals with dimensions of 0·1 × 0·1 × 0·1 mm were used. The Weissenberg photographs of TPE and DTM were taken at −160°C, whereas the NaCl reflexion spots were obtained at room temperature. For the calculation of the cell dimensions for TPE, 108 0*kl* and 59 *h*0*l* reflexions were available, and for DTM, 167 0*kl* and 109 *h*0*l* reflexions.

Table 1. *Crystallographic data of TPE and DTM at* −160°C

TPE, $C_{26}H_{20}$, $M=332{\cdot}5$
Monoclinic, $a=9{\cdot}798$ (2), $b=9{\cdot}175$ (2), $c=10{\cdot}781$ (2) Å, $\beta=107{\cdot}94$ (1)°, $V=1019$ Å^3, space group $P2_1$ (from systematic absences and piezoelectricity), $Z=2$, D_m (20°C) = 1·1, $D_c(-160°\text{C})=1{\cdot}08$ g cm^{-3}, $F(000)=352$, $\mu(\text{Mo } K\alpha)=0{\cdot}66$ cm^{-1}

DTM, $C_{31}NH_{25}$, $M=411{\cdot}5$
Monoclinic, $a=8{\cdot}195$ (1), $b=17{\cdot}659$ (1), $c=16{\cdot}970$ (2) Å, $\beta=118{\cdot}08$ (1)°, $V=2167$ Å^3, space group $P2_1/c$ (from systematic extinctions), $Z=4$, D_m(20°C) = 1·2, $D_c(-160°\text{C})=1{\cdot}26$ g cm^{-3}, $F(000)=872$, $\mu(\text{Mo } K\alpha)=0{\cdot}78$ cm^{-1}

The intensities were measured on an AD-3 Nonius diffractometer in essentially the same way as described in paper I for TPH. For none of the reference reflexions was the change in intensity larger than 4%. Details of the intensity measurements are given in Table 2.

Determination and refinement of the structures

For TPE and DTM the distribution of the E values appeared to be acentric and centric respectively, in agreement with the space groups given in Table 1. Both compounds have one independent molecule at a general position in the unit cell. Models of the structures were found by direct methods. Use was made of the $\sum_1$ and $\sum_2$ relationships and of the tangent formula (Karle & Karle, 1966). For TPE with space group $P2_1$

the phases obtained appeared to be approximately (within 5°) equal to 0 or 180°, as expected (Schenk, 1972). From an E map calculated in space group $P2_1/m$, which contains the structure plus its inverse, a model for the TPE structure in space group $P2_1$ could readily be deduced. For DTM no difficulties were encountered.

The structures of TPE and DTM have been refined in essentially the same way as described for TPH in paper I. Details are given in Table 2. For TPE, space group $P2_1$, the origin along y is not fixed by symmetry. Although none of the y coordinates was kept constant, no difficulties were encountered during the block-diagonal refinement (see also Rollett, 1965). In the

Table 2. *Details of the intensity measurements and structure refinements of TPE and DTM*

	TPE	DTM
Crystal size (mm)	0·50 × 0·37 × 0·15	0·6 × 0·3 × 0·3
External form	Block	Block, rough edges
Mosaic spread	< 0·5	< 0·5
φ axis	[010]	[010]
Radiation (filter)	Mo(Zr)	Mo(Zr)
Scanning method	θ–2θ	θ–2θ
Scanning range (°)	0·72 + 0·5 tg θ	0·74 + 0·5 tg θ
Counter opening (°)	1·34	1·39
$(\sin\theta)/\lambda$ (Å^{-1})	0–0·847	0–0·885
Reference reflexions	222; 321	162; $30\bar{8}$
Number of independent $I(hkl)$'s measured	4924	12372
Number of $\lvert F(hkl)\rvert$'s used in refinement (N_o)	4477*	11253*–26
Number of variables (N_v)	256	315
Weighting scheme w	$[\sigma^2 + \lvert 0{\cdot}03F_o\rvert^2]^{-1}$	$[\sigma_c^2 + \lvert 0{\cdot}04F_o\rvert^2]^{-1}$
N_o/N_v	17·49	35·64
$R_w(R)$ (%)†	8·47 (10·36)	8·19 (7·49)
Goodness-of-fit G‡	1·24	1·24

* Intensities with $I(\text{net}) > 0$ accepted.

† $R_w = [\{\sum w(\lvert F_o\rvert - \lvert F_c\rvert)^2\}/\sum w\lvert F_o\rvert^2]^{1/2}$.

‡ $G = [\{\sum w(\lvert F_o\rvert - \lvert F_c\rvert)^2\}/(N_o - N_v)]^{1/2}$.

Table 3. *TPE: final coordinates and thermal parameters*

For the numbering of the atoms, see Fig. 2.

(*a*) Fractional coordinates and anisotropic thermal parameters (× 10⁴) for the non-hydrogen atoms. The temperature factor is $T(hkl) = \exp[-2\pi^2(U_{11}a^{*2}h^2 + U_{22}b^{*2}k^2 + U_{33}c^{*2}l^2 + 2U_{12}ha^*kb^* + 2U_{23}kb^*lc^* + 2U_{13}ha^*lc^*)]$.

	x	y	z	U_{11}	U_{22}	U_{33}	$2U_{12}$	$2U_{23}$	$2U_{13}$
C(1)	0·37847 (35)	0·23097 (42)	0·28128 (25)	415 (16)	390 (18)	131 (10)	−296 (30)	−2 (23)	120 (20)
C(2)	0·31866 (30)	0·29707 (38)	0·36822 (26)	237 (12)	350 (16)	191 (11)	−184 (24)	108 (23)	−38 (18)
C(3)	0·39202 (26)	0·29541 (32)	0·50068 (23)	174 (10)	230 (12)	137 (9)	−84 (18)	35 (18)	72 (15)
C(4)	0·52824 (24)	0·23184 (29)	0·54884 (21)	176 (9)	165 (10)	136 (9)	−79 (18)	−18 (17)	122 (15)
C(5)	0·58773 (30)	0·16749 (32)	0·46000 (26)	270 (12)	213 (12)	213 (11)	−92 (21)	−121 (20)	215 (19)
C(6)	0·51243 (38)	0·16767 (38)	0·32668 (27)	469 (18)	318 (16)	211 (13)	−292 (29)	−197 (23)	386 (25)
C(7)	0·32578 (28)	0·12806 (36)	0·92322 (26)	191 (10)	317 (15)	213 (11)	−4 (21)	103 (22)	230 (18)
C(8)	0·40109 (27)	0·25922 (34)	0·94241 (24)	204 (10)	300 (14)	167 (10)	29 (21)	−4 (20)	189 (17)
C(9)	0·48917 (25)	0·29245 (30)	0·86690 (23)	165 (9)	198 (11)	167 (9)	13 (18)	2 (18)	133 (15)
C(10)	0·50271 (24)	0·19552 (27)	0·77177 (21)	115 (8)	173 (10)	123 (8)	−11 (15)	6 (16)	93 (13)
C(11)	0·42435 (26)	0·06595 (30)	0·75090 (24)	160 (9)	195 (11)	165 (10)	−88 (18)	−14 (18)	84 (15)
C(12)	0·33699 (28)	0·03128 (33)	0·82766 (26)	179 (10)	230 (12)	224 (11)	−48 (19)	84 (20)	135 (18)
C(13)	0·60124 (24)	0·22955 (27)	0·69284 (21)	154 (9)	126 (10)	140 (9)	6 (16)	−3 (16)	109 (14)
C(14)	0·74218 (24)	0·25821 (27)	0·75137 (22)	154 (9)	152 (10)	134 (8)	−22 (16)	30 (16)	106 (14)
C(15)	0·93435 (29)	0·21208 (39)	1·16482 (25)	217 (12)	373 (17)	177 (11)	202 (23)	166 (23)	33 (18)
C(16)	0·95952 (28)	0·33634 (37)	1·10200 (26)	191 (11)	313 (15)	183 (11)	13 (21)	−29 (21)	2 (17)
C(17)	0·89754 (27)	0·34969 (32)	0·96688 (24)	166 (10)	223 (12)	181 (10)	−34 (18)	25 (18)	82 (16)
C(18)	0·80995 (23)	0·23886 (29)	0·89456 (21)	132 (8)	173 (10)	143 (9)	24 (17)	52 (17)	59 (14)
C(19)	0·78925 (26)	0·11316 (33)	0·95900 (26)	158 (10)	217 (12)	235 (11)	36 (19)	150 (20)	64 (17)
C(20)	0·85039 (29)	0·10084 (36)	1·09379 (27)	211 (11)	301 (15)	226 (12)	141 (22)	270 (22)	90 (18)
C(21)	1·02774 (29)	0·43030 (35)	0·55510 (26)	239 (11)	248 (13)	212 (11)	−147 (21)	−61 (21)	242 (19)
C(22)	0·88964 (30)	0·48716 (34)	0·52890 (26)	243 (12)	232 (13)	204 (11)	−92 (21)	101 (20)	136 (19)
C(23)	0·79632 (26)	0·43157 (31)	0·59109 (24)	164 (10)	191 (11)	192 (10)	17 (18)	38 (19)	94 (16)
C(24)	0·83864 (23)	0·31602 (27)	0·67954 (22)	134 (9)	138 (10)	170 (9)	1 (16)	25 (16)	125 (15)
C(25)	0·97854 (25)	0·26061 (30)	0·70559 (23)	159 (9)	174 (11)	179 (10)	28 (17)	5 (17)	111 (15)
C(26)	1·07206 (25)	0·31755 (32)	0·64395 (25)	142 (9)	230 (12)	234 (11)	−14 (18)	−100 (20)	180 (17)

Table 3 (*cont.*)

(*b*) Fractional coordinates and isotropic thermal parameters for the hydrogen atoms

	x	*y*	*z*	*B*
H(C1)	0·32083	0·23062	0·17885	4·2 (10)
H(C2)	0·21304	0·34856	0·33272	3·3 (9)
H(C3)	0·34427	0·34578	0·56772	1·9 (7)
H(C5)	0·69335	0·11600	0·49550	2·5 (8)
H(C6)	0·56018	0·11730	0·25964	3·9 (9)
H(C7)	0·25812	0·10297	0·98190	4·0 (10)
H(C8)	0·39202	0·33485	1·01682	2·0 (7)
H(C9)	0·54878	0·39402	0·88246	2·5 (8)
H(C11)	0·43342	−0·00968	0·67649	2·5 (8)
H(C12)	0·27738	−0·07029	0·81210	2·0 (7)
H(C15)	0·98269	0·20139	1·26888	3·6 (9)
H(C16)	1·02625	0·42283	0·15723	3·2 (9)
H(C17)	0·91628	0·44681	0·91746	2·9 (8)
H(C19)	0·72252	0·02667	0·90377	2·5 (8)
H(C20)	0·83165	0·00372	1·14321	1·9 (7)
H(C21)	1·10111	0·47497	0·50730	3·5 (9)
H(C22)	0·85449	0·57594	0·45994	2·4 (8)
H(C23)	0·68954	0·47589	0·57093	2·7 (8)
H(C25)	1·01369	0·17183	0·77455	1·8 (7)
H(C26)	1·17884	0·27323	0·66411	2·5 (7)

final stages of the refinement of DTM 26 very weak reflexions with $w|\Delta|^2 > 30$ were discarded. In Table 3 the final parameters of TPE with their standard deviations

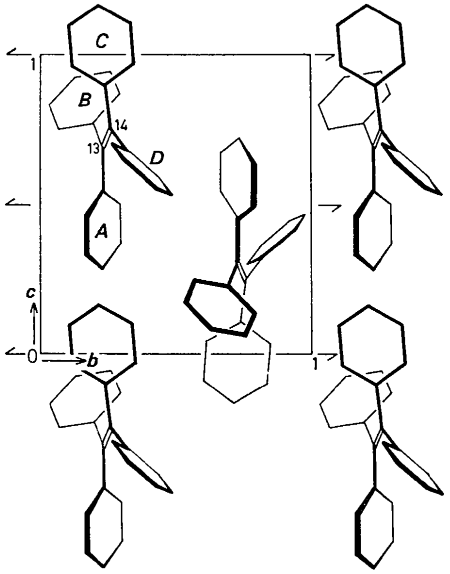

Fig. 1. TPE. Projection of the structure along [100] onto the plane (100). The centres of the phenyl groups lie at heights $x=0·45$ (*A*), 0·41 (*B*), 0·87 (*C*) and 0·93 (*D*). The middle of the double bond C(13)–C(14) lies at height 0·67.

Table 4. *DTM: final coordinates and thermal parameters*

For the numbering of the atoms, see Fig. 4.

(*a*) Fractional coordinates and anisotropic thermal parameters ($\times 10^4$) for the non-hydrogen atoms.

	x	*y*	*z*	U_{11}	U_{22}	U_{33}	$2U_{12}$	$2U_{23}$	$2U_{13}$
C(1)	0·39911 (13)	0·43208 (5)	0·12773 (6)	117 (3)	114 (3)	92 (3)	0 (5)	−11 (5)	92 (5)
C(2)	0·21561 (13)	0·43940 (6)	0·05986 (6)	119 (3)	156 (4)	104 (3)	28 (6)	−2 (6)	67 (6)
C(3)	0·16978 (14)	0·42957 (6)	−0·02938 (7)	164 (4)	158 (4)	104 (4)	24 (6)	−10 (6)	61 (6)
C(4)	0·30747 (15)	0·41382 (6)	−0·05336 (7)	211 (4)	159 (4)	110 (4)	1 (7)	−23 (6)	129 (7)
C(5)	0·49013 (15)	0·40812 (6)	0·01277 (7)	188 (4)	172 (4)	125 (4)	15 (6)	−10 (6)	180 (7)
C(6)	0·53537 (13)	0·41682 (6)	0·10268 (6)	136 (4)	139 (4)	118 (4)	3 (6)	−0 (6)	132 (6)
C(7)	0·65312 (12)	0·44523 (5)	0·28738 (6)	93 (3)	114 (3)	98 (3)	−15 (5)	−9 (5)	82 (5)
C(8)	0·74651 (13)	0·37552 (5)	0·30811 (6)	109 (3)	127 (4)	130 (4)	10 (5)	1 (6)	98 (6)
C(9)	0·93614 (13)	0·37125 (6)	0·36516 (7)	109 (3)	179 (4)	154 (4)	52 (6)	22 (6)	99 (6)
C(10)	1·03746 (13)	0·43683 (6)	0·40324 (7)	97 (3)	218 (5)	146 (4)	−21 (6)	−3 (7)	80 (6)
C(11)	0·94650 (14)	0·50615 (6)	0·38333 (7)	117 (4)	180 (4)	155 (4)	−71 (6)	−16 (6)	93 (6)
C(12)	0·75684 (13)	0·51052 (6)	0·32569 (7)	114 (3)	136 (4)	131 (4)	−43 (6)	−19 (6)	94 (6)
C(13)	0·35082 (12)	0·52171 (5)	0·22650 (6)	101 (3)	104 (3)	95 (3)	7 (5)	−7 (5)	70 (5)
C(14)	0·22679 (13)	0·53047 (5)	0·26092 (6)	116 (3)	127 (4)	102 (3)	30 (5)	3 (5)	93 (6)
C(15)	0·14628 (14)	0·60089 (6)	0·25853 (7)	143 (4)	148 (4)	121 (4)	72 (6)	−6 (6)	104 (6)
C(16)	0·18658 (15)	0·66340 (6)	0·22103 (7)	189 (4)	122 (4)	148 (4)	74 (6)	−3 (6)	109 (7)
C(17)	0·30643 (15)	0·65529 (6)	0·18448 (7)	195 (4)	108 (4)	162 (4)	4 (6)	18 (6)	137 (7)
C(18)	0·38702 (14)	0·58516 (6)	0·18710 (7)	149 (4)	115 (4)	141 (4)	5 (6)	26 (6)	135 (6)
C(19)	0·22775 (12)	0·33026 (5)	0·19181 (6)	99 (3)	110 (3)	103 (3)	−24 (5)	−31 (5)	86 (5)
C(20)	0·04242 (13)	0·33607 (6)	0·17276 (7)	102 (3)	151 (4)	163 (4)	−25 (6)	−59 (6)	106 (6)
C(21)	−0·08855 (14)	0·28571 (6)	0·11316 (7)	110 (4)	188 (4)	201 (4)	−54 (6)	−70 (7)	106 (7)
C(22)	−0·03606 (15)	0·22962 (6)	0·07168 (7)	156 (4)	170 (4)	178 (4)	−113 (6)	−106 (7)	107 (7)
C(23)	0·14840 (15)	0·22329 (6)	0·09123 (7)	175 (4)	147 (4)	174 (4)	−69 (6)	−117 (6)	166 (7)
C(24)	0·28052 (13)	0·27293 (6)	0·15182 (7)	117 (3)	128 (4)	155 (4)	−23 (6)	−62 (6)	126 (6)
C(25)	0·41180 (12)	0·36817 (5)	0·34565 (6)	97 (3)	98 (3)	95 (3)	7 (5)	−1 (5)	84 (5)
C(26)	0·36209 (13)	0·29964 (5)	0·37159 (6)	145 (4)	108 (3)	136 (4)	−23 (6)	18 (6)	130 (6)
C(27)	0·40611 (14)	0·28619 (6)	0·46033 (7)	163 (4)	128 (4)	155 (4)	2 (6)	75 (6)	146 (7)
C(28)	0·50585 (14)	0·33886 (6)	0·52681 (7)	135 (4)	161 (4)	119 (4)	35 (6)	67 (6)	103 (6)
C(29)	0·55908 (13)	0·40596 (5)	0·50225 (6)	104 (3)	138 (4)	100 (3)	17 (5)	4 (5)	75 (5)
C(30)	0·51177 (12)	0·42112 (5)	0·41373 (6)	111 (3)	110 (3)	100 (3)	−2 (5)	−7 (5)	92 (5)
C(31)	0·44170 (12)	0·44488 (5)	0·22591 (6)	86 (3)	101 (3)	93 (3)	1 (5)	2 (5)	74 (5)
N(32)	0·36183 (11)	0·38125 (4)	0·25544 (5)	107 (3)	104 (3)	95 (3)	−54 (5)	−19 (5)	81 (5)

Table 4 (*cont.*)

(*b*) Fractional atomic coordinates and isotropic thermal parameters for the hydrogen atoms

	x	y	z	B
H(C2)	0·11027	0·45136	0·07797	1·7 (3)
H(C3)	0·02912	0·43441	−0·08022	2·1 (4)
H(C4)	0·27204	0·40681	−0·12317	2·3 (4)
H(C5)	0·59550	0·39615	−0·00532	2·1 (3)
H(C6)	0·67611	0·41200	0·15354	1·8 (3)
H(C8)	0·66941	0·32526	0·27916	1·9 (3)
H(C9)	0·00501	0·31777	0·38032	2·5 (4)
H(C10)	0·18538	0·43362	0·44787	2·0 (3)
H(C11)	0·02362	0·55645	0·41233	1·6 (3)
H(C12)	0·68798	0·56403	0·31057	2·3 (3)
H(C14)	0·19612	0·48236	0·29034	1·2 (3)
H(C15)	0·05345	0·60692	0·28600	2·0 (3)
H(C16)	0·12324	0·71805	0·21895	2·7 (4)
H(C17)	0·33715	0·70338	0·15510	2·0 (4)
H(C18)	0·47989	0·57914	0·15965	2·2 (4)
H(C20)	0·00166	0·37953	0·20418	2·1 (3)
H(C21)	−0·23046	0·29059	0·09827	2·2 (4)
H(C22)	−0·13783	0·19078	0·02528	2·3 (4)
H(C23)	0·18917	0·17986	0·05981	2·2 (4)
H(C24)	0·42242	0·26807	0·16669	1·5 (3)
H(C26)	0·28609	0·25862	0·32120	1·5 (3)
H(C27)	0·36543	0·23432	0·47824	2·2 (4)
H(C28)	0·54218	0·32762	0·59652	2·4 (4)
H(C29)	0·63514	0·44697	0·55263	1·5 (3)
H(C30)	0·55246	0·47299	0·39582	1·1 (3)

as calculated by the block-diagonal least-squares program are given. In Table 4 the corresponding parameters for DTM are listed. To check whether the values of the standard deviations are affected by the block-diagonal approximation, a full-matrix refinement was carried out for TPE. In this case the y coordinate of C(1) was kept fixed. Apart from y[C(1)] hardly any differences were observed between the two sets of standard deviations.*

For bond lengths and angles not involving H atoms the standard deviations (for calculation see paper I) are 0·003 Å and 0·25° for TPE and 0·001 Å and 0·09° for DTM. No corrections for libration have been applied as for both compounds these corrections are equal to or smaller than the estimated standard deviations.

Description of the crystal structure

The packing of the molecules

The packing of the molecules in TPE is shown in Figs. 1 and 2. Fig. 1 shows that to a good approximation the C=C bonds are parallel to **a*** and lie in the planes $y=\frac{1}{4}$ and $y=\frac{3}{4}$. In Table 5 the distances shorter than the relevant sum of the van der Waals distances are listed.

The packing of the molecules in DTM is shown in Figs. 3 and 4, and short intermolecular distances in Table 5. From Fig. 3 it is seen that the points of intersection of the screw axes of type $[\frac{1}{2},y,\frac{1}{4}]$ and $[\frac{1}{2},y,\frac{3}{4}]$ with the xz plane form a lattice consisting of approximately equilateral triangles. Along each of these screw axes a column of DTM molecules is found (see also Fig. 4). Within each of the columns there is only one intermolecular distance which is shorter than the van der Waals distance, *viz.* the H···H distance of 2·319 Å in Table 5. The relative location of the molecules in neighbouring columns is such that in [100] projection again a lattice of equilateral triangles is formed; in this case the N atoms of the molecules coincide with the corners of the triangles. Between neighbouring columns there are shorter intermolecular distances than within a column. The shortest C···C distance (3·29 Å) is found between the centrosymmetrically related rings A and A' shown in Fig. 4.

Conformation of the molecules; thermal motion

The conformation of the molecules will be discussed in paper III (Hoekstra & Vos, 1975). In the present

Table 5. *Short intermolecular distances* (Å) *in TPE and DTM*

Distances shorter than the sum of the relevant van der Waals radii [1·7 for C, 1·5 for N and 1·2 Å for H (Pauling, 1960)] are given. For an explanation of the symmetry code see Table 6 of paper I.

I. TPE; symmetry-operations: (1) x,y,z; (2) $\bar{x},y+\frac{1}{2},\bar{z}$

C(26)···H(C22)	64502	2·680	H(C22)···H(C26)	65502	2·214
C(20)···H(C17)	64602	2·722	H(C3)····H(C26)	45501	2·278
C(26)···H(C20)	65602	2·782	H(C1)····H(C8)	55401	2·281
C(16)···H(C12)	55602	2·882	H(C2)····H(C16)	45401	2·294
			H(C1)····H(C7)	54401	2·335
			H(C8)····H(C19)	55602	2·384

II. DTM; symmetry operations: (1) x,y,z; (2) $\bar{x},\bar{y},\bar{z}$; (3) $\bar{x},y+\frac{1}{2},\frac{1}{2}-z$; (4) $x,\frac{1}{2}-y,\frac{1}{2}+z$

C(5)····C(5)	66502	3·288	C(16)·····H(C28)	66602	2·841
			C(14)·····H(C29)	66602	2·843
C(4)····H(C27)	55404	2·668	C(14)·····H(C3)	56502	2·852
C(5)····H(C27)	55404	2·674	C(28)·····H(C10)	45501	2·860
C(15)···H(C3)	56502	2·742	C(29)·····H(C22)	65504	2·886
C(29)···H(C10)	45501	2·794	C(10)·····H(C14)	65501	2·890
C(16)···H(C3)	56502	2·800			
C(30)···H(C29)	66602	2·802	H(C9)····H(C16)	64503	2·319
C(11)···H(C15)	65501	2·833	H(C2)····H(C3)	56502	2·327

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30937 (62 pp., 2 microfiches). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

section the thermal motions of TPE and DTM will be compared with each other and with that of TPH at −160 °C (paper I, Hoekstra *et al.*, 1975). For each of the molecules we have calculated the r.m.s. value $U'=\langle U_{ii}^2(m)\rangle^{1/2}$ of the lengths of the main axes of the thermal ellipsoids of the heavy atoms. From the U' values given in Table 6 it is seen that the thermal parameters are in the order TPH > TPE > DTM. This increase in thermal parameters corresponds to an increase in length of both the shortest intra- and intermolecular distances in the three compounds (intermolecular distances are given in Table 5 of the present paper and in Table 6 of paper I; intramolecular distances are listed in Tables 1, 2 and 3 of paper III, distances between atoms linked to the same atom are not considered). For each of the molecules a rigid-body analysis according to Cruickshank (1956) with refinement of the origin of the libration axes (Pawley, 1963)

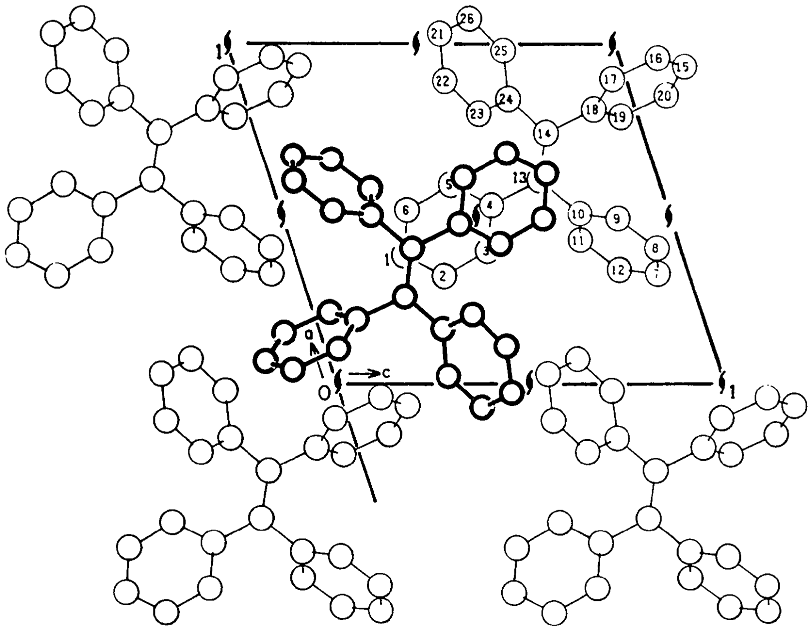

Fig. 2. TPE. Projection of the structure along [010] onto the plane (010). The middle of the double bond C(13)–C(14) lies at height $y=0{\cdot}24$.

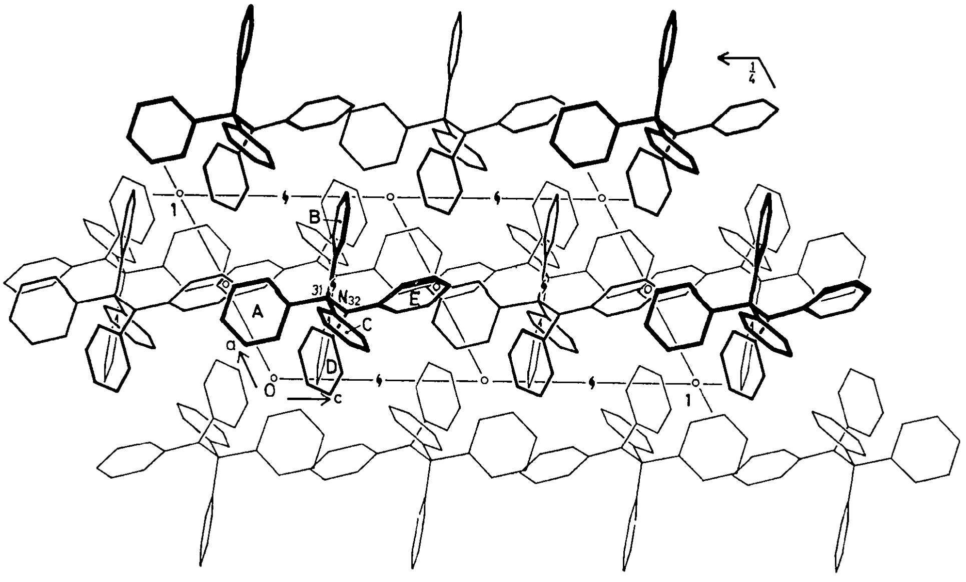

Fig. 3. DTM. Projection of the structure along [010] onto the plane (010). The middle of the central bond C(31)–N(32) lies at height $y=0{\cdot}41$. The centres of the phenyl rings lie at heights 0·42 (*A*), 0·45 (*B*), 0·59 (*C*), 0·28 (*D*) and 0·35 (*E*).

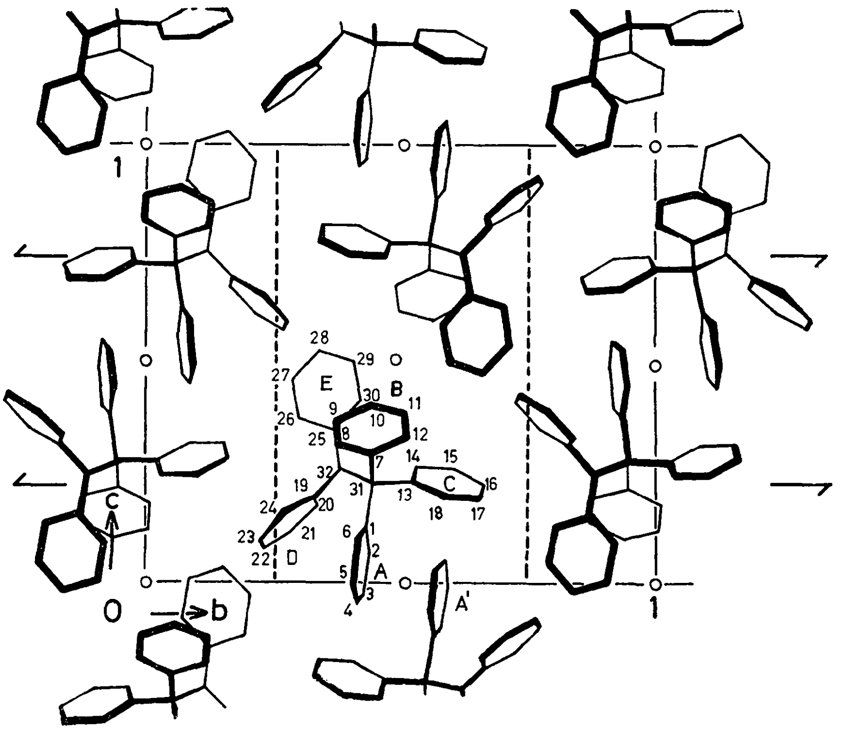

Fig. 4. DTM. Projection of the structure along [100] onto the plane (100).

has been performed. As a measure for the flexibility of the molecules we have taken

$$D=[\sum\{U_{ij}(\mathrm{obs})-U_{ij}(\mathrm{calc})\}^2/(6N-9)]^{1/2}$$

with $N=26$ for TPE and 32 for DTM. The D values and the r.m.s. standard deviations $\sigma(\mathrm{r.m.s.})=\langle\sigma^2[U_{ii}(\mathrm{obs})]\rangle^{1/2}$ are listed in Table 6. The table shows that the flexibility of the molecules is in the same order (TPH$\rangle$TPE$\rangle$DTM) as the values of the thermal parameters U' and the lengths of the shortest intra- or intermolecular distances. For TPH it should be noted that the thermal parameters may be affected by a slight disorder. This disorder may be due to impurities (indicated by the green colour of the crystals; Forrester, Hay & Thompson, 1968) or to a possible dissociation of the molecules by the incident X-rays (see paper I for the influence of ultraviolet light).

Table 6. *Thermal parameters* (Å^2) *of TPH, TPE and DTM at* −160°C

For definition of symbols, see text.

	TPH	TPE	DTM
U'	0·0408	0·0227	0·0142
D	0·0052	0·0032	0·0011
σ(r.m.s.)	0·0013	0·0011	0·0004

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