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# The Crystal and Molecular Structures of Tetraphenylhydrazine and Related Compounds at −160°C. I. The Crystal Structure and Physical Properties of Tetraphenylhydrazine (TPH)

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The crystal structure of tetraphenylhydrazine (TPH) has been determined at room temperature and at −160°C. The two structures show no essential differences. The data at −160°C are: space group $C222_1$, $a=35\cdot400$ (15), $b=12\cdot616$ (7), $c=12\cdot120$ (8) Å, $Z=12$. The cell contains α molecules at general positions and β molecules at special positions with symmetry 2. Direct methods failed to solve the structure, but a model could be obtained by the Patterson search method. For the anisotropic refinement by the block-diagonal least-squares technique 4758 independent reflexion intensities, measured with Zr-filtered Mo radiation on an AD-3 diffractometer, were available. $R_w=6\cdot10\%$. The N–N bond is 1·406 (4) Å, The average value for the angles C–N–C (126·7°) is considerably larger than for the angles N–N–C (116·5°). The phenyl torsion angles φ range from 9·7 to 40·5° and the angle of twist around the N–N bonds is 74·1°. The structure obtained is used to discuss the photodissociation of TPH molecules into diphenylamino radical dimers which occurs on irradiation of TPH crystals with ultraviolet light at 77°K.

## Introduction

E.s.r. spectra of crystalline tetraphenylhydrazine (TPH) irradiated with ultraviolet light have been studied at temperatures between 77 and 300°K by Wiersma, Lichtenbelt & Kommandeur (1969) and by Shida & Kira (1969). These studies have shown that on irradiation at 77°K approximately 1‰ of the molecules dissociate into diphenylamino (DPA) radical dimers by the reaction

$$(C_6H_5)_2N\text{-}N(C_6H_5)_2 \xrightarrow{\text{uv}} 2\cdot N(C_6H_5)_2\cdot$$

The dissociation–recombination process appears to be reversible. To explain the e.s.r. spectra obtained as a function of ultraviolet wavelength and of temperature, Wiersma *et al.* (1969) assumed two crystallographically independent molecules (α and β) to be present in the crystal with orthorhombic symmetry $C222_1$. The α molecules dissociate into α dimers (of which there are two magnetically different types) with no internal symmetry and with ·N– –N· approximately perpendicular to **b**. The β molecules give β dimers (six magnetically different types) with twofold symmetry and ·N– –N· perpendicular to **a** (Table 9). The α molecules appeared to dissociate at longer wavelengths ($\lambda=$ 3650 Å) than the β molecules ($\lambda\simeq$ 3000 Å), whereas its dimers recombine more readily at 77°K than those of the β molecules. Wiersma *et al.* have tentatively ascribed this difference in behaviour to a difference in surroundings of the molecules. To check the assumptions made, we have determined the crystal structure at room temperature and at −160°C.

Since the conformation observed for the TPH molecules appeared to be different from the conformation expected by Wiersma & Kommandeur (1967), we became interested in a comparative study of the conformation of TPH and related compounds. The molecules considered are summarized in the introduction to the second paper of this series (Hoekstra & Vos, 1975*a*). Their conformations are discussed in the third paper (Hoekstra & Vos, 1975*b*).

## Experimental

The compound was kindly provided by Dr D. A. Wiersma (Laboratory of Physical Chemistry of this University). Light green crystals were obtained by slow evaporation from a solution in a 1:1 mixture of toluene and chloroform. The crystal structure has been determined at room temperature and at −160°C. There is no phase transition in this temperature range. The crystallographic data are given in Table 1. The cell dimensions at 20°C were determined from the θ values obtained from Weissenberg photographs of zero-layer lines taken with Cu radiation and calibrated with NaCl reflexion spots. The best values of the cell dimensions were calculated with a least-squares procedure from the observed $(\sin^2\theta)/\lambda^2$ values, each value having a weight $1/(\sin^2 2\theta)[\lambda(\text{Cu } K\alpha_1)=1\cdot54050, \lambda(\text{Cu } K\alpha_2)=1\cdot54434$ Å, $a(\text{NaCl}, 21\,°\text{C})=5\cdot64006$ Å]. Use was made of 118 $hk0$ and 45 $0kl$ reflexions. The cell dimensions at −160 °C were calculated from the $2\theta$ values of the reflexions 30,0,0; 32,0,0; 080; 0,14,0; 004 and 006. These $2\theta$ values were measured on a Nonius AD-3 diffractometer with Mo $K\alpha$ radiation ($\lambda = 0{\cdot}7107$ Å).

Table 1. *Crystallographic data on TPH at* 20 °C *and* −160 °C

Tetraphenylhydrazine, $C_{24}N_2H_{20}$, $M = 336{\cdot}5$, orthorhombic, space group $C222_1$, $Z = 12$, $F(000) = 2136$

| | 20 °C | −160 °C |
|---|---|---|
| $a$ | 35·590 (10) Å | 35·400 (15) Å |
| $b$ | 12·736 (5) | 12·616 (7) |
| $c$ | 12·044 (4) | 12·120 (8) |
| $V$ | 5459 Å$^3$ | 5413 Å$^3$ |
| $\mu$(Cu $K\alpha$) | 5·46 cm$^{-1}$ | 5·69 cm$^{-1}$ |
| $\mu$(Mo $K\alpha$) | 0·78 cm$^{-1}$ | 0·79 cm$^{-1}$ |
| $d$(obs) | 1·2 g cm$^{-3}$ | |
| $d$(calc) | 1·23 g cm$^{-3}$ | 1·24 g cm$^{-3}$ |

The intensities were measured on the diffractometer with Zr-filtered Mo radiation. The $\theta$–$2\theta$ scanning method was applied. For the measurements at −160 °C the crystal was cooled in a stream of cold nitrogen gas (van Bolhuis, 1971). Every two hours a reference reflexion was measured three times; the average intensities of the sets of three reflexions were used to make corrections for variations in the intensity of the primary beam and for possible changes in the reflecting power of the crystal. For none of the reference reflexions was the fluctuation in intensity larger than 4%. Deviations from linearity of the scintillation counter were kept smaller than 1% by the use of attenuation filters. The intensities were corrected for Lorentz and polarization effects, but not for absorption. For each reflexion with $I(\text{net}) > 0$ the variance $\sigma_c^2$ due to counting statistics and, where applicable, to the error in the attenuation factor was calculated. Details of the intensity measurements are given in Table 2.

## Determination of the structure

The structure was derived from the room-temperature data, which were available first. The space group $C222_1$ has an eightfold general position. The 12 molecules in the cell can be divided into a group of eight molecules (at a general position) plus a group of four molecules (with twofold symmetry), or into three groups of four molecules. In the latter case there will probably be two independent molecules around **a** and one molecule around **b** as **a** is considerably larger than **b**. With the assumption that the symmetry elements of the space group $C222_1$ are retained on dissociation, the e.s.r. work of Wiersma *et al.* (see *Introduction*) strongly suggests that there is one molecule at a special position around **a** with N–N perpendicular to **a**, plus one molecule at a general position with N–N approximately perpendicular to **b** (see also Table 9).

### *Visual inspection of the Patterson synthesis and direct methods*

Despite the information obtained from the e.s.r. work many difficulties were encountered in finding the structure. Neither visual inspection of a sharpened Patterson synthesis combined with trial and error with the strong reflexions 022 ($E = 3{\cdot}97$), 620 ($E = 3{\cdot}79$) and 602 ($E = 3{\cdot}03$), nor application of direct methods gave a good model. In the latter case use was made of the $\sum_1$ (Karle & Hauptman, 1956; Weeks & Hauptman, 1970) and $\sum_2$ relationships and of the tangent formula (Karle & Karle, 1966; Germain & Woolfson, 1968; Germain, Main & Woolfson, 1970, 1971; Hall, 1970). When the structure was known (see below) it appeared that some phases which had been found with high statistical significance (Cochran, 1955) at the beginning of the phase determination were in error. Because of the difficulties described above, the structure

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

| | 20 °C | −160 °C |
|---|---|---|
| Crystal size (mm) | ~0·4 × 0·4 × 0·4 | 0·4 × 0·4 × 0·4 |
| External form | Pyramid | Cube |
| Mosaic spread (°) | < 0·3 | < 0·4 |
| $\varphi$ axis | [001] | [001] |
| Radiation (filter) | Mo(Zr) | Mo(Zr) |
| Scanning method | $\theta$–$2\theta$ | $\theta$–$2\theta$ |
| Scanning range (°) | $0{\cdot}52 + 0{\cdot}5 \operatorname{tg} \theta$ | $0{\cdot}70 + 0{\cdot}5 \operatorname{tg} \theta$ |
| Counter aperture (°) | 0·94 | 1·29 |
| $(\sin \theta)/\lambda$ (Å$^{-1}$) | 0–0·595 | 0–0·746 |
| Reference reflexions | 772; 932; 14,2,2 | 772; 932; 14,2,2 |
| Number of independent $I(hkl)$'s measured | 2702* | 5151 |
| Number of $\lvert F(hkl)\rvert$'s used in refinement ($N_o$) | 1995†–3 | 4761†–3 |
| Number of variables ($N_v$) | 383 | 383 |
| Weighting scheme | $w = 1$ | $w = [\sigma_c^2 + 0{\cdot}0003\lvert F_o\rvert^2]^{-1}$ |
| $N_o/N_v$ | 5·20 | 12·42 |
| $R_w(R)$ (%)‡ | $R = 5{\cdot}48$ | 6·10 (7·13) |
| Goodness-of-fit $G$§ | 2·05 | 1·55 |

* At 20 °C a range selector was used.

† At 20 °C: intensities with $w_c > 0{\cdot}10\ \bar{w}_c$ accepted. At −160 °C: intensities with $I(\text{net} > 0$ accepted.

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

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

is at present being used as a test case for the development of direct methods computer programs such as *MULTAN* (Main, 1974).

### *Patterson search*

The structure was solved by the second group of authors by their automatic Patterson search method (Braun, Hornstra & Leenhouts, 1969). The Patterson synthesis was sharpened by multiplication of $|F(hkl)|^2$ by $\sin^2 \theta/f_c(hkl)$. As a search model the rigid $C_6$–N unit occurring in the TPH molecule was used. The number of atoms in this model (seven) is considerably smaller than the number $\sqrt{156} \simeq 13$ (square root of the number of atoms in the primitive unit cell) required for a good chance of solving the structure (Braun, Hornstra & Leenhouts, 1969). The search yielded 21 possible orientations. Starting from these 21 models and models related to them by rotation around the three twofold axes and by inversion, we attempted first to locate the molecule at a special position (or possibly the three molecules at special positions). To this end, we tested which pairs of $C_6$–N groups could be combined to form a $C_6$–N–$C_6$ group with a reasonable angle C–N–C (between 110 and 150°) and reasonable intramolecular distances. Further we checked which of the $C_6$–N–$C_6$ groups obtained gave rise to a molecule with acceptable geometry when placed with N at $(\frac{1}{2} \times 1{\cdot}4)$ Å from a twofold axis parallel to **a** or **b**. The possibility of N–N being parallel to **a** or **b** was not considered because it would be in disagreement with the e.s.r. data.

After optimization, good agreement with the Patterson synthesis was obtained for the vector sets of one molecule around **a** and three (approximately identical) molecules around **b**. A second molecule around **a** could be found only by accepting an angle C–N–C of 107°. For each of the five molecules with known orientation a translation search along the respective twofold axis was made to check whether a position could be found for which the vector set of the pair of symmetry-related molecules showed good agreement with the Patterson map. As this appeared to be the case

Table 3. *Final coordinates* ($\times 10^5$) *of the heavy atoms in TPH*

For numbering scheme, see Fig. 1. Standard deviations, in units of the last decimal place, are given in parentheses.

| | −160°C | | | | 20°C | | |
|---|---|---|---|---|---|---|---|
| | *x* | *y* | *z* | | *x* | *y* | *z* |
| C(1) | −10554 (7) | 1835 (22) | 33250 (22) | C(1) | −10555 (15) | 1658 (53) | 33079 (50) |
| C(2) | −11491 (7) | −4233 (20) | 23976 (22) | C(2) | −11487 (15) | −4186 (45) | 23903 (48) |
| C(3) | −9449 (7) | −3394 (20) | 14168 (21) | C(3) | −9454 (15) | −3406 (42) | 14115 (44) |
| C(4) | −6405 (6) | 3681 (19) | 13471 (20) | C(4) | −6440 (13) | 3605 (41) | 13472 (41) |
| C(5) | −5399 (6) | 9561 (20) | 22893 (21) | C(5) | −5421 (13) | 9340 (44) | 22825 (43) |
| C(6) | −7479 (7) | 8646 (22) | 32616 (21) | C(6) | −7501 (15) | 8497 (50) | 32411 (46) |
| N(7) | −4349 (5) | 4507 (17) | 3400 (17) | N(7) | −4370 (11) | 4419 (34) | 3402 (35) |
| C(8) | 2546 (8) | 30065 (24) | −6587 (25) | C(8) | 2383 (18) | 29896 (52) | −6563 (55) |
| C(9) | −487 (8) | 31766 (20) | 486 (26) | C(9) | −653 (17) | 31521 (47) | 501 (59) |
| C(10) | −2839 (7) | 23514 (21) | 3636 (22) | C(10) | −2950 (15) | 23178 (47) | 3647 (46) |
| C(11) | −2092 (6) | 13181 (21) | −2 (22) | C(11) | −2147 (12) | 13064 (43) | 11 (47) |
| C(12) | 887 (7) | 11541 (21) | −7461 (22) | C(12) | 840 (15) | 11499 (45) | −7313 (48) |
| C(13) | 3136 (7) | 19963 (25) | −10731 (24) | C(13) | 3023 (17) | 19860 (56) | −10604 (53) |
| C(14) | 32817 (9) | 24238 (23) | 57751 (24) | C(14) | 32726 (20) | 24224 (52) | 57694 (52) |
| C(15) | 35436 (8) | 26154 (21) | 49590 (28) | C(15) | 35318 (17) | 26129 (48) | 49647 (67) |
| C(16) | 35089 (7) | 21634 (19) | 39081 (23) | C(16) | 35010 (16) | 21755 (42) | 39105 (50) |
| C(17) | 32012 (6) | 14980 (18) | 36716 (21) | C(17) | 31987 (13) | 15174 (39) | 36860 (44) |
| C(18) | 29375 (7) | 12921 (21) | 45087 (21) | C(18) | 29377 (14) | 12863 (43) | 45095 (43) |
| C(19) | 29748 (8) | 17653 (23) | 55509 (23) | C(19) | 29741 (18) | 17601 (52) | 55462 (51) |
| N(20) | 31735 (5) | 10209 (15) | 26144 (17) | N(20) | 31740 (11) | 10399 (32) | 26230 (35) |
| C(21) | 22571 (7) | −7032 (21) | 12951 (24) | C(21) | 22634 (15) | −6721 (47) | 13240 (49) |
| C(22) | 21930 (6) | 2053 (22) | 19162 (23) | C(22) | 22001 (14) | 2188 (50) | 19336 (52) |
| C(23) | 24913 (7) | 7995 (18) | 23571 (21) | C(23) | 24961 (15) | 8207 (42) | 23735 (49) |
| C(24) | 28593 (6) | 4492 (18) | 21862 (19) | C(24) | 28595 (13) | 4705 (37) | 22059 (40) |
| C(25) | 29249 (7) | −4562 (20) | 15455 (21) | C(25) | 29230 (14) | −4252 (42) | 15717 (47) |
| C(26) | 26266 (8) | −10251 (21) | 10969 (23) | C(26) | 26285 (17) | −9925 (46) | 11230 (50) |
| C(27) | 33380 (8) | 34347 (23) | −6128 (24) | C(27) | 33454 (17) | 33814 (52) | −6170 (54) |
| C(28) | 31356 (7) | 34912 (21) | 3714 (24) | C(28) | 31422 (16) | 34539 (46) | 3514 (56) |
| C(29) | 31837 (7) | 27300 (19) | 11914 (22) | C(29) | 31881 (15) | 27117 (41) | 11912 (48) |
| C(30) | 34399 (6) | 18991 (18) | 10407 (20) | C(30) | 34416 (13) | 18826 (40) | 10530 (45) |
| C(31) | 36365 (6) | 18193 (20) | 340 (22) | C(31) | 36358 (14) | 17823 (46) | 452 (49) |
| C(32) | 35878 (7) | 25966 (23) | −7814 (21) | C(32) | 35886 (16) | 25393 (53) | −7791 (46) |
| N(33) | 34818 (5) | 11238 (16) | 18895 (17) | N(33) | 34791 (10) | 11356 (33) | 19106 (35) |
| C(34) | 44564 (7) | −6374 (21) | 26817 (24) | C(34) | 44460 (14) | −5989 (48) | 27184 (54) |
| C(35) | 44853 (6) | 2619 (22) | 20347 (23) | C(35) | 44764 (13) | 2782 (47) | 20658 (49) |
| C(36) | 41689 (6) | 8638 (20) | 17689 (22) | C(36) | 41633 (14) | 8679 (44) | 18018 (46) |
| C(37) | 38122 (6) | 5443 (18) | 21528 (19) | C(37) | 38078 (13) | 5634 (39) | 21793 (41) |
| C(38) | 37846 (6) | −3421 (19) | 28450 (21) | C(38) | 37823 (14) | −3093 (42) | 28800 (48) |
| C(39) | 41061 (7) | −9268 (21) | 31027 (24) | C(39) | 41006 (16) | −8880 (48) | 31459 (54) |

only for the first molecule around **a**, the conclusion was reached that the cell contains one molecule at a special position around **a** and thus one molecule at a general position. In the search for the molecule at a general position it was assumed that both $C_6$–N–$C_6$ units of this molecule would not differ too much from the $C_6$–N–$C_6$ group of the molecule at a special position. An orientation search with this $C_6$–N–$C_6$ unit followed by a translation search gave, besides the molecule already located, two acceptable $C_6$–N–$C_6$ groups at general positions in the unit cell. The two groups could be combined to form a molecule with reasonable geometry and with a vector set that showed good agreement with the Patterson map.

In the model obtained, the molecule at a special position has N–N perpendicular to **a** whereas the molecule at a general position has N–N approximately perpendicular to **b** (see Table 9). This agrees with the ·N– –N· directions observed by Wiersma *et al.* (1969) for the $\beta$ and $\alpha$ dimers respectively. The $\alpha$ molecule at a general position contains a pseudo-twofold axis parallel to $y$ at $z=\frac{1}{4}$ (equal to the $z$ value of the real twofold axis $[0,y,\frac{1}{4}]$). This pseudosymmetry (see also Hornstra, 1970) explains why the orientation search pointed to the presence of a molecule with twofold symmetry around **b**. Owing to the presence of two other symmetry elements, the search with the unit of 13 atoms could overcome this difficulty.

## Refinement of the structure

For both the room- and low-temperature data refinement was by block-diagonal least-squares calculations (Cruickshank, 1961). Some numerical data of the refinements are given in Table 2. For C and N scattering factors of Doyle & Turner (1968) were used and for H that of Stewart, Davidson & Simpson (1965). The H atoms of the phenyl groups were put at geometrically reasonable positions with C–H constrained to 1·08 Å. For the heavy atoms anisotropic temperature factors and for H isotropic temperature factors were used. Three very strong reflexions (022, 620 and 602) which appeared to suffer from extinction were omitted. The value of $\alpha^2=0.0003$ in the weighting scheme $w=[\sigma_c^2+\alpha^2|F_o|^2]^{-1}$ of the low-temperature data was chosen such as to keep $\langle w|\Delta|^2\rangle$ as a function of $|F_o|$ as constant as possible. In Table 3 the final coordinates of the heavy atoms at 20 and at −160 °C are listed. In Table 4 the coordinates of the H atoms at −160 °C are given with the values of the parameters $B$ of the isotropic temperature factors. Table 5 shows the thermal parameters of the heavy atoms at −160 °C.*

Table 4. *Final coordinates* (× $10^5$) *and B values* (*in* Å$^2$) *for the hydrogen atoms at* −160 °C

| | $x$ | $y$ | $z$ | $B$ |
|---|---|---|---|---|
| H(C1) | −12189 | 1233 | 40747 | 4·9 (7) |
| H(C2) | −13842 | −9673 | 24421 | 4·5 (6) |
| H(C3) | −10212 | −8185 | 7128 | 4·2 (6) |
| H(C5) | −2996 | 14826 | 22589 | 3·5 (6) |
| H(C6) | −6690 | 13289 | 39739 | 3·1 (5) |
| H(C8) | 4408 | 36501 | −8810 | 4·7 (7) |
| H(C9) | −1020 | 39653 | 3580 | 3·9 (6) |
| H(C10) | −5243 | 25048 | 8885 | 4·1 (6) |
| H(C12) | 1426 | 3695 | −10657 | 2·9 (6) |
| H(C13) | 5383 | 18634 | −16598 | 4·8 (7) |
| H(C14) | 33137 | 27797 | 65801 | 5·0 (7) |
| H(C15) | 37812 | 31258 | 51331 | 4·5 (7) |
| H(C16) | 37180 | 23260 | 32818 | 4·9 (7) |
| H(C18) | 27035 | 7644 | 43495 | 3·7 (6) |
| H(C19) | 27653 | 16191 | 61807 | 5·1 (7) |
| H(C21) | 20227 | −11537 | 9703 | 4·0 (6) |
| H(C22) | 19060 | 4595 | 20626 | 3·0 (5) |
| H(C23) | 24367 | 15147 | 28201 | 4·3 (7) |
| H(C25) | 32113 | −7150 | 13987 | 4·5 (7) |
| H(C26) | 26813 | −17158 | 5953 | 5·8 (8) |
| H(C27) | 33016 | 40349 | −12392 | 5·2 (8) |
| H(C28) | 29389 | 41337 | 4999 | 5·2 (7) |
| H(C29) | 30226 | 27816 | 19462 | 2·5 (5) |
| H(C31) | 38247 | 11599 | −1103 | 4·3 (6) |
| H(C32) | 37447 | 25452 | −15437 | 5·1 (7) |
| H(C34) | 47035 | −11100 | 28580 | 3·5 (6) |
| H(C35) | 47589 | 5016 | 17298 | 3·9 (6) |
| H(C36) | 41972 | 15700 | 12721 | 3·6 (6) |
| H(C38) | 35138 | −5715 | 31786 | 3·9 (6) |
| H(C39) | 40832 | −16109 | 36341 | 5·2 (7) |

Table 3 shows that there are no essential differences between the structures at room and at low temperature. Therefore, apart from a comparison of the bond lengths observed at 20 and at −160 °C (see below), only the more accurate low-temperature structure will be discussed. The conformation of the molecules will be discussed in paper III. The discussion of the thermal parameters will be given in paper II. Corrections for libration have not been applied, as at low temperature these corrections are equal to or smaller than the standard deviations of the atomic coordinates.

## Description of the structure at −160°C

### *Packing of the molecules*

The packing of the molecules is shown in Figs. 1 and 2. The cell contains one set of eight $\alpha$ molecules at general positions and one set of four $\beta$ molecules on twofold axes. In Table 6 short intermolecular distances are given. When comparing these distances with the sum of the relevant van der Waals radii it should be taken into account that the radius of H can assume values from 1·0 to 1·4 Å (Nyburg, 1961).

From Fig. 1 it is seen that the structure contains columns parallel to **c** consisting either of $\alpha$ or $\beta$ molecules. Successive molecules in an $\alpha$ column are related by the symmetry operations of twofold axes of type $[x,0,0]$ or $[x,0,\frac{1}{2}]$. For a $\beta$ column the symmetry axes are of type $[0,y,\frac{1}{4}]$ and $[0,y,\frac{3}{4}]$. In addition to this the $\beta$ column, in which the molecules lie on twofold axes

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* A list of observed and calculated structure factors for the structure determination at −160° has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30936 (27 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 5. *Thermal parameters* (×10⁴) *of the carbon and nitrogen atoms nitrogen atoms at* −160°C

The temperature factor is $T(hkl)=\exp\left[-2\pi^2(U_{11}a^{*2}h^2+U_{22}b^{*2}k^2+U_{33}c^{*2}l^2+2U_{12}ha^*kb^*+2U_{23}kb^*lc^*+2U_{13}ha^*lc^*)\right]$.

| | $U_{11}$ | $U_{22}$ | $U_{33}$ | $2U_{12}$ | $2U_{23}$ | $2U_{13}$ |
|---|---|---|---|---|---|---|
| C(1) | 436 (14) | 449 (16) | 350 (14) | 192 (25) | −1 (25) | 49 (23) |
| C(2) | 380 (13) | 389 (13) | 383 (14) | 37 (23) | −53 (26) | −29 (23) |
| C(3) | 349 (12) | 369 (13) | 342 (13) | 55 (21) | −114 (24) | −53 (21) |
| C(4) | 256 (10) | 355 (12) | 306 (12) | 121 (19) | −155 (23) | −72 (19) |
| C(5) | 277 (11) | 416 (13) | 345 (14) | 123 (21) | −165 (24) | −122 (20) |
| C(6) | 439 (14) | 448 (15) | 301 (13) | 199 (25) | −195 (25) | −113 (23) |
| N(7) | 343 (10) | 404 (11) | 351 (11) | −75 (18) | −313 (20) | 91 (18) |
| C(8) | 531 (17) | 460 (16) | 478 (16) | −60 (28) | 274 (29) | −127 (29) |
| C(9) | 530 (15) | 405 (14) | 446 (15) | 72 (28) | −28 (27) | −204 (29) |
| C(10) | 368 (13) | 441 (15) | 368 (14) | 103 (24) | −92 (26) | −134 (23) |
| C(11) | 290 (10) | 415 (13) | 303 (11) | 44 (22) | −94 (23) | −119 (21) |
| C(12) | 348 (13) | 465 (15) | 378 (14) | 142 (23) | −8 (26) | 48 (23) |
| C(13) | 400 (14) | 602 (18) | 415 (15) | 95 (28) | 178 (31) | 92 (26) |
| C(14) | 734 (20) | 452 (16) | 414 (16) | 455 (31) | −205 (28) | −480 (31) |
| C(15) | 517 (15) | 327 (13) | 600 (17) | 175 (25) | −168 (27) | −512 (31) |
| C(16) | 348 (12) | 307 (12) | 492 (15) | 85 (21) | −8 (24) | −269 (25) |
| C(17) | 305 (11) | 256 (11) | 367 (13) | 119 (19) | 36 (21) | −128 (21) |
| C(18) | 397 (13) | 362 (13) | 346 (13) | 127 (23) | 16 (23) | −60 (22) |
| C(19) | 569 (17) | 502 (17) | 356 (15) | 309 (29) | 10 (27) | −141 (27) |
| N(20) | 224 (9) | 341 (10) | 334 (10) | −56 (16) | −51 (19) | 23 (17) |
| C(21) | 384 (14) | 426 (15) | 423 (15) | −230 (24) | −3 (26) | −53 (24) |
| C(22) | 255 (11) | 481 (16) | 465 (15) | −33 (22) | 20 (28) | 49 (23) |
| C(23) | 276 (11) | 333 (12) | 347 (13) | 35 (20) | −45 (22) | −1 (20) |
| C(24) | 237 (10) | 270 (11) | 323 (12) | −69 (18) | 79 (21) | −49 (18) |
| C(25) | 303 (11) | 350 (12) | 406 (14) | 22 (21) | −95 (24) | 41 (21) |
| C(26) | 494 (15) | 372 (14) | 383 (14) | −88 (25) | −175 (26) | 50 (26) |
| C(27) | 455 (15) | 474 (16) | 488 (16) | −253 (27) | 286 (29) | −296 (27) |
| C(28) | 381 (13) | 326 (13) | 559 (17) | −71 (22) | 120 (27) | −290 (25) |
| C(29) | 312 (12) | 298 (12) | 417 (14) | −75 (20) | 1 (23) | −145 (23) |
| C(30) | 257 (11) | 298 (11) | 336 (12) | −134 (19) | 23 (21) | −128 (20) |
| C(31) | 320 (11) | 397 (13) | 348 (12) | −193 (22) | 5 (24) | −151 (23) |
| C(32) | 386 (14) | 547 (16) | 351 (14) | −277 (26) | 95 (27) | −131 (23) |
| N(33) | 223 (9) | 338 (11) | 394 (11) | −14 (17) | 108 (19) | 62 (17) |
| C(34) | 281 (12) | 445 (15) | 501 (17) | 113 (23) | 89 (28) | −61 (24) |
| C(35) | 248 (11) | 496 (16) | 438 (15) | −59 (22) | 24 (27) | −16 (22) |
| C(36) | 279 (12) | 358 (13) | 387 (13) | −84 (21) | 91 (23) | −28 (21) |
| C(37) | 223 (10) | 300 (11) | 348 (13) | −13 (18) | −19 (21) | 1 (19) |
| C(38) | 281 (11) | 349 (13) | 448 (15) | −33 (20) | 146 (25) | 29 (22) |
| C(39) | 349 (12) | 370 (14) | 484 (15) | 41 (22) | 193 (26) | 1 (24) |

Table 6. *Short intermolecular distances* (Å) *at* −160°C

For C···H and H···H, distances shorter than the sum of the relevant van der Waals radii (1·7 Å for C and 1·2 Å for H; Pauling, 1960) are listed. For C···C, distances shorter than 3·40+0·30=3·70 Å are given. Column 1: atoms involved. The first atom is taken directly from Tables 3 or 4. The second atom is obtained from the corresponding atom listed in Tables 3 or 4 by the operation given by the code in column 2. Translations in the *x*, *y* and *z* directions are equal to the first, second or third digit respectively, minus 5; the last two digits give the symmetry operation applied (Johnson, 1965).

Symmetry operations: (1) $x,y,z$; (2) $x,-y,-z$; (3) $-x,-y,\frac{1}{2}+z$; (4) $-x,y,\frac{1}{2}-z$; (5) $x+\frac{1}{2},y+\frac{1}{2},z$; (6) $x+\frac{1}{2},-y+\frac{1}{2},-z$; (7) $-x+\frac{1}{2},-y+\frac{1}{2},\frac{1}{2}+z$; (8) $-x+\frac{1}{2},y+\frac{1}{2},\frac{1}{2}-z$.

| α···α | Code | Length | β···β | Code | Length |
|---|---|---|---|---|---|
| C(18)···C(18) | 55602 | 3·471 | C(6)···C(12) | 55503 | 3·658 |
| C(14)···C(38) | 55602 | 3·587 | C(6)···H(C12) | 55503 | 2·771 |
| C(25)···C(31) | 55502 | 3·601 | H(C5)···H(C5) | 55504 | 2·200 |
| C(21)···C(21) | 55502 | 3·606 | H(C1)···H(C1) | 55602 | 2·264 |
| C(25)···C(32) | 55502 | 3·695 | | | |
| C(14)···C(22) | 55507 | 3·699 | α···β | | |
| C(31)···H(C25) | 55502 | 2·687 | C(9)···C(35) | 45506 | 3·602 |
| C(15)···H(C21) | 55508 | 2·775 | C(2)···C(29) | 44505 | 3·625 |
| C(14)···H(C38) | 55602 | 2·783 | C(3)···C(27) | 45506 | 3·629 |
| C(32)···H(C25) | 55502 | 2·823 | C(8)···C(35) | 55407 | 3·665 |
| C(16)···H(C21) | 55508 | 2·841 | C(29)···H(C2) | 55505 | 2·709 |
| C(15)···H(C39) | 55602 | 2·857 | C(9)···H(C35) | 45506 | 2·809 |
| C(19)···H(C38) | 55602 | 2·878 | C(6)···H(C15) | 45606 | 2·861 |
| H(C34)···H(C34) | 65504 | 2·272 | C(8)···H(C35) | 45506 | 2·882 |
| H(C22)···H(C27) | 55507 | 2·277 | C(35)···H(C8) | 55507 | 2·887 |
| | | | C(1)···H(C15) | 45606 | 2·894 |
| | | | H(C6)···H(C15) | 45606 | 2·331 |

parallel to **a**, contains a twofold screw axis parallel to **c**. In [001] projection each α column is surrounded by two β and two α columns, whereas each β column is surrounded by four α columns.

From Table 6 it can be seen that the shortest intermolecular distances occur within an α column (see distances with symmetry operation 2). Table 1 in paper III shows that in the α molecules the phenyl torsion angles vary from 9·7 to 40·5° and the angles N–N–C from 115·2 to 118·1°. For the β molecules these variations are considerably smaller: the phenyl torsion angles vary from 23·7 to 25·3° and the angles N–N–C from 116·3 to 117·1°. The relatively small variations observed for the β molecules combined with the fact that the β molecules are surrounded at larger distances by their neighbours than the α molecules, indicate that the β molecules approach the 'idealized form' more closely than the α molecules. In view of this it is reasonable to assume that the packing of the α molecules is energetically less favorable than that of the β molecules.

### *Conformation of the molecules*

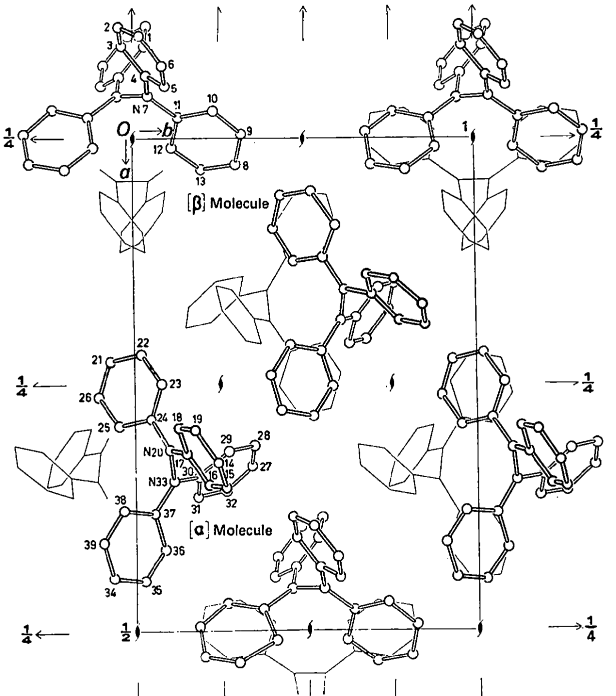


Fig. 1. Projection of the structure along [001] onto the plane (001). Because of the *C*-centring only half the unit-cell is given. The centres of the N(7)–N(7′) (β molecule) and N(20)–N(31) (α molecule) bonds lie at heights $z=0$ and $z=0{\cdot}23$ respectively. The α molecule having the centre of N–N at $z=-0{\cdot}27$ and the β molecule with N–N at $z=-\frac{1}{2}$ are drawn with thin lines.

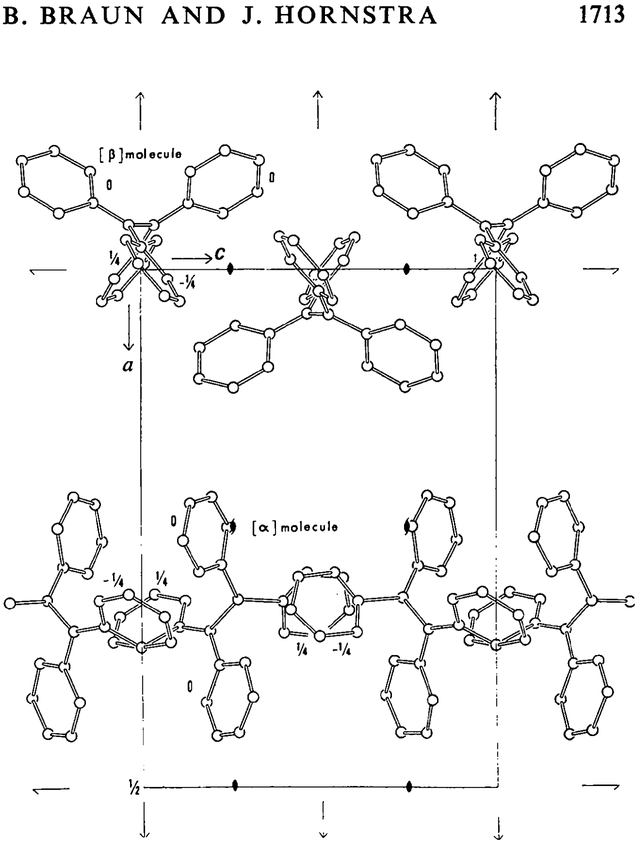


Fig. 2. Projection of the structure along [010] onto the plane (010). The *b* axis points downwards. Only the α column (see text) around the line $[\frac{1}{4},0,z]$ and the β column are given. For some of the phenyl rings the heights *y* are indicated roughly by $-\frac{1}{4}$, 0 or $\frac{1}{4}$.

Table 7. *Average values for bond lengths* (Å) *and angles* (°) *of the TPH molecules at room and at low temperature*

| | −160°C | | 20°C | |
|---|---|---|---|---|
| | α | β | α | β |
| ⟨C–C⟩ | 1·396 | 1·395 | 1·388 | 1·388 |
| ⟨C–N⟩ | 1·422 | 1·421 | 1·418 | 1·420 |
| N–N | 1·407 | 1·404 | 1·389 | 1·390 |
| ⟨C–N–C⟩ | 126·9 | 126·4 | 126·1 | 126·3 |
| ⟨N–N–C⟩ | 116·5 | 116·7 | 116·9 | 116·8 |
| ⟨φ⟩ | 24·3 | 24·5 | 24·6 | 24·8 |
| θ | 74·0 | 74·2 | 74·3 | 74·4 |

Some characteristic features of the molecules at 20 and −160°C are given in Table 7 (values of individual bond lengths and angles are given in Fig. 2 and Table 1 of paper III). The standard deviations in the bond lengths and angles were calculated from the variance-covariance matrices of the least-squares refinement (Darlow, 1960). For bond lengths and angles not involving H atoms the values obtained are 0·004 Å and 0·27° for the low-temperature and 0·008 Å and 0·50° for the room-temperature structure. Table 7 shows that at room temperature the observed bond lengths have a tendency to be shorter than at low temperature. We ascribe this shortening to libration effects. The discussion of the conformation of the molecules in paper III will be based on the bond lengths and angles observed at −160 °C. For the discussion of the physical properties in the present paper it is sufficient to note that the observed conformation with $\varphi$ values varying from 9·7 to 40·5° is very different from the conformation assumed by Wiersma *et al.* (1967) for the interpretation of their e.s.r. spectra ($\varphi = 90°$, Fig. 3).

## Discussion of the physical properties

The diphenylamino (DPA) radical dimers formed on dissociation of TPH molecules can be in a singlet or a triplet state. The lines observed in the e.s.r. spectrum are split because of the magnetic dipole interaction of the unpaired electrons (Wiersma, 1969). The line splitting depends on the orientation of the second-order spin–spin interaction tensor $\Lambda$ relative to the magnetic field vector **H**. In Table 8 the number of non-equivalent orientations of $\Lambda$ relative to **H**, and thus the number of doublets to be expected for each type of radical dimer, is given for different directions of **H**. In finding the numbers listed in the table it has been assumed that after dissociation the different dimers of the same type are still related by the symmetry elements of the space group $C222_1$. Moreover it is supposed that each $\beta$ dimer still has the twofold symmetry of the original molecule. Interpretation of the spectra revealed that there are two types of $\alpha$ dimer ($\alpha_1$ and $\alpha_2$) and six types of $\beta$ dimer ($\beta_1$ to $\beta_6$). In Table 9 a summary of the experimental data is given. The zero-field splitting parameters $D$ and $E$ given in the table are related directly to the main axes $X$, $Y$ and $Z$ of the tensor $\Lambda$: $X = D/3 - E$, $Y = D/3 + E$ and $Z = -2D/3$. As $E$ is much smaller than $D$ the main axes $X$ and $Y$ are approximately equal and $Z$ is expected to coincide with ·N– –N· in good approximation. As can be seen from Table 9, the ·N– –N· directions obtained from the e.s.r. spectra show good agreement with the directions of the N–N bonds in the molecules as found by the present X-ray diffraction study. This strongly suggests that dissociation takes place in the bulk of the crystals and not at dislocations or defects. From the two sets of $D$ values of approximately 0·022 and 0.012 cm$^{-1}$ Wiersma *et al.* have calculated ·N– –N· distances of 2·7 and 4·0 Å respectively for the radical dimers. These distances are likely to be in error, however, as the present work has shown that the conformation of the dimers on which the calculation was based is not correct. In view of the two categories of $D$ values (and thus of ·N– –N· distances) observed, Wiersma *et al.* have proposed a two-step stretching dissociation mechanism (Fig. 4; for more detailed arguments, see Wiersma *et al.*, 1969). For the conformation with $\varphi = 90°$ adopted in their work the proposed $\alpha_1$ (or $\beta_1$) dimer with ·N– –N· = 2·7 Å, is sterically possible. This is no longer true, however, for the present conformation with $\langle\varphi\rangle = 25°$. Therefore the proposed two-step stretching dissociation mechanism with ·N– –N· = 2·7 Å for $\alpha_1$ (or $\beta_1$) is not possible for the observed crystal structure.

Table 8. *Number of doublets* for each type of $\alpha$ or $\beta$ dimer*

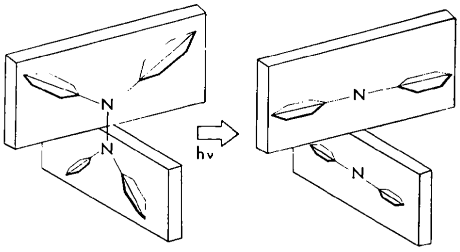
For the $\beta$ dimers one of the main axes of the tensor $\Lambda$ coincides with the twofold $a$ axis.

| Direction of **H** | $\alpha$ | $\beta$ |
|---|---|---|
| General | 4 | 2 |
| Parallel to (100) | 2 | 2 |
| Parallel to (010) or (001) | 2 | 1 |
| Parallel to [100], [010] or [001] | 1 | 1 |

* The numbers given by Wiersma *et al.* (1969) are not correct. Errors occur because only 8 ($4\alpha + 4\beta$) molecules were assumed to be present per cell and dimers related by the $C$-centring were not considered as magnetically equivalent. Their interpretation of the e.s.r. spectra remains correct, however, as some of the errors cancel. Moreover the twofold symmetry assumed for the $\alpha$ molecules was not adopted for the $\alpha$ dimers in the crystal.

Why $\beta$ molecules require light with shorter wave length than do $\alpha$ molecules for their dissociation has not been explained yet. In the crystals the packing of the $\alpha$ molecules seems to be energetically less favorable than that of the $\beta$ molecules (see previous section). The energy required to initiate the dissociation is connected, however, with the activation energy of the process involved, which energy cannot directly be deduced from the static crystal structure. Further theoretical work is in progress in our laboratory.

Thanks are due to Dr D. A. Wiersma for valuable discussions and to Mr F. van Bolhuis, Mr. H. Zoer and



(a) (b)

Fig. 3. Conformation assumed by Wiersma & Kommandeur (1967) for (a) the TPH molecule, and (b) the DPA radical dimer; $\varphi = 90°$. According to Wiersma *et al.* (1969) the angle $\theta$ may deviate from 90°.

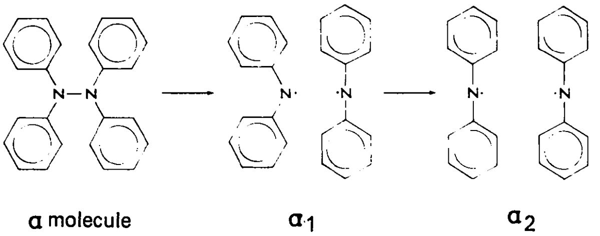
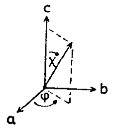


Fig. 4. Two-step dissociation mechanism for TPH assumed by Wiersma *et al.* (1969). For $\alpha_1$ ·N– –N· = 2·7, for $\alpha_2$ ·N– –N· = 4·0 Å. A linear configuration was supposed to be favorable for the DPA groups.

Table 9. *Experimental data for the radical dimers*

$D$ (in $10^{-2}$ cm$^{-1}$) and $E$ (in $10^{-4}$ cm$^{-1}$) are the zero-field splitting parameters. The angles $\chi(Z)$ and $\varphi(Z)$ give the direction of the main axis $Z$ of the tensor $\Lambda$, which axis is assumed to coincide with $\cdot$N– –N$\cdot$ (see text). The angles $\chi(m)$ and $\varphi(m)$ give the directions of N–N in the molecules.

| Radicals | $D$ | $E$ | $\lambda$ (abs)* | $\chi$ ($Z$) | $\varphi$ ($Z$) | $\chi$ ($m$) | $\varphi$ ($m$) |
|---|---|---|---|---|---|---|---|
| $\alpha_1$ | 2·416 | 6·56 | 6000 Å | 49·5 | −5·2 | 51·4 | −6·8 |
| $\alpha_2$ | 1·164 | 5·0 | 7500 | 52·3 | 5·5 | | |
| $\beta_1$ | 2·41 | 5·4 | 5600 | 59 | 90 | 54·1 | 90 |
| $\beta_3$ | 2·24 | 7·5 | | 54 | 90 | | |
| $\beta_5$ | 2·15 | <7·5 | | | | | |
| $\beta_2$ | 1·25 | 2·2 | 8000 | 60 | 90 | | |
| $\beta_4$ | 1·21 | 7·5 | | 60 | 90 | | |
| $\beta_6$ | 1·21 | <7·5 | | 60 | 90 | | |



* In visible absorption spectrum.

Mrs S. C. Swen for help during part of the experimental work. Attempts to solve the structure were made by Dr Tiny Spoelder and Drs A. Dijkstra. The computations were carried out at the Computing Centre of the University of Groningen.

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