

The Crystal Structure of a 2,2-Diphenyl-1-picrylhydrazyl (DPPH) Modification

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X-ray diffraction data, collected with a diffractometer, were used to determine the structure of 2,2-diphenyl-1-picrylhydrazyl (DPPH) at -160°C . Crystals of the DPPH modification studied are triclinic, space group $P\bar{1}$, $Z=4$, with $a=13.571$ (7), $b=19.102$ (10), $c=7.370$ (2) Å, $\alpha=92.88$ (6), $\beta=101.92$ (3) and $\gamma=95.67$ (8) $^{\circ}$. The structure was solved by direct methods. Least-squares refinement of 11750 independent observed reflexions with $\sin \theta/\lambda > 0.4$ Å $^{-1}$ led to an R_w of 0.107. The conformations of the two independent molecules are roughly the same as the conformation of the DPPH molecules in DPPH-benzene, with approximate sp^2 hybridization for both central N atoms. For the central N-N bond, values of 1.334 and 1.349 Å are observed. Strain in the molecule is released by bending of valence angles and large torsions of the phenyl and picryl groups. The sum of the torsion angles of the two

phenyl rings with the approximately planar N-N  skeleton is in all cases 69° . In the structure, channels are present around the lines $[0, \frac{1}{2}, z]$ where solvent molecules (probably acetone) are accommodated. There is little overlap between adjacent radicals in the crystal structure.

Introduction

The stable, free radical 2,2-diphenyl-1-picrylhydrazyl (DPPH) has been the subject of a large number of investigations (see *Physical properties*). DPPH is known in several forms (Weil & Anderson, 1965), some of which were reported to be solvent free. Of the latter, DPPH-I (m.p. 106°C) is orthorhombic (Williams, 1965), DPPH-II (m.p. 137°C) is amorphous and DPPH-III (m.p. 128 – 129°C) is triclinic (Williams, 1965). The only structure determination was by Williams (1967) on DPPH-benzene. The present paper describes the structure determination at -160°C of a DPPH modification, which on the basis of its cell dimensions was thought to be isomorphous with DPPH-III studied by Williams (1965). It turned out, however, that our compound contains molecules of the solvent from which it was crystallized and it will therefore be indicated as DPPH-IIIa.

Experimental

DPPH in powder form (m.p. 126 – 130°C) is commercially available (EGA-chemie). Crystals of DPPH-IIIa (m.p. 127 – 128°C) were grown from a solution of DPPH in a mixture of acetone and petroleum spirit (1:4) by slow evaporation of the solvents. Results of elemental analyses are given in Table 1, and indicate the possibility of the presence of acetone molecules in the crystals, which will be discussed later.

Weissenberg photographs showed the crystals to be triclinic. As no piezoelectric effect was observed, the

Table 1. Results of elemental analyses for DPPH-IIIa

	% C	% H	% N	% O
Calculated				
DPPH	54.8	3.1	17.8	24.3
DPPH. $\frac{1}{2}$ acetone	55.1	3.3	17.1	24.5
DPPH. $\frac{1}{2}$ acetone	55.3	3.5	16.5	24.6
Experimental				
Average values	55.2	3.4	16.8	
r.m.s. error	0.51	0.14	0.17	

space group was assumed to be $P\bar{1}$, which proved to be correct during the structure refinement. The cell contains, apart from the solvent molecules, two independent DPPH molecules. All accurate measurements were made on a three-circle automatic Nonius diffractometer with Zr-filtered Mo radiation; $\lambda(\text{Mo } K\alpha) = 0.71069$ Å. A crystal $0.4 \times 0.35 \times 0.2$ mm was used both for the determination of the cell constants and for the intensity measurements. The crystal was cooled to -160°C by a cold stream of nitrogen gas (van Bolhuis, 1971). Cell dimensions were found by least-squares adjustments to θ , φ and χ angles of 28 reflexions. In Table 2 the values obtained are compared with the room-temperature values of DPPH-III (Williams, 1965). The similarity in cell constants strongly suggests that our material is isostructural with Williams's DPPH. The latter compound cannot contain acetone (or petroleum spirit), however, as it was crystallized from carbon disulphide (Weil & Anderson, 1965).

All independent reflexions up to $\sin \theta/\lambda = 0.81$ Å $^{-1}$ were measured by the moving crystal/moving counter method. Deviations from linearity of the scintillation

Table 2. *Crystal data of DPPH-IIIa*

Williams's (1965) results for DPPH-III are also given.			
Present work	Williams (1965)		
-160°C	room temperature		
<i>a</i>	13.571 (7) Å	13.58 (1) Å	Triclinic
<i>b</i>	19.102 (10)	18.91 (1)	Space group: <i>P</i> $\bar{1}$
<i>c</i>	7.370 (2)	7.555 (5)	Formula without solvent
α	92.88 (6)°	92.2 (1)°	molecules: C ₁₈ H ₁₂ N ₅ O ₆
β	101.92 (3)	101.6 (1)	F.W. 394
γ	95.67 (8)	95.0 (1)	<i>Z</i> = 4
<i>V</i>	1855 Å ³	1890 Å ³	<i>d</i> _c = 1.41 g cm ⁻³

counting equipment were kept below 1% by attenuation filters. At intervals of approximately 2 h a reference reflexion was measured. Corrections were made for intensity changes in the primary beam and for Lorentz and polarization effects, but not for absorption [$\mu(\text{Mo}) = 0.3 \text{ cm}^{-1}$]. Reflexions with a negative net intensity were given zero weight. For the remaining 13661 reflexions a weight w_c was calculated according to $w_c = [\sigma_c(F)]^{-2}$, $\sigma_c(F)$ being the standard deviation in F due to counting statistics and errors in the filter factors (only for reflexions measured with an attenuation filter).

Determination of the structure

Solution of the phase problem

The data were brought onto an absolute scale by Wilson statistics and E values were calculated. With the program *AUDICE* (Spek, 1968, 1975) the structure was solved. This program generated 3346 triples $E_h E_k E_{h+k}$ from 664 reflexions with $E > 1.85$. The origin was fixed with the three reflexions $12, \bar{3}, \bar{3}$, $3, 10, 8$ and $12, 3, \bar{2}$. Another 25 reflexions were added to the starting set and assigned symbolic phases. The phases of the remaining reflexions were expressed in terms of the 25 symbols. In every step the most reliable phase relation was used. The next step taken by the program was the elimination with statistically reliable relations

of 19 symbols, so that six were left. Each of these symbols determined the phases of approximately half of the 643 phases determined with the phasing procedure. The resulting set of 64 solutions was then ordered with the criterion: $\sum_{h,k} s_h s_k s_{h+k} |E_h E_k E_{h+k}|$.

Fourier syntheses calculated for several of the more probable solutions did not reveal the structure. At this point we examined the steps taken by the program during the elimination process more closely. This suggested the following procedure: prevent the symbolic phase assigned to the reflexion $7, \bar{1}, \bar{3}, 2$ from being eliminated, so that the associated symbolic relation, formerly used in the elimination, will be skipped in spite of its high probability and frequent occurrence. This intervention appeared to be successful. The symbolic relation considered was later shown to be false. The Fourier synthesis, calculated for the third solution ordered according to the above criterion, showed all the atoms of the two independent molecules.

Refinement

The positions and anisotropic temperature factors of C, N and O were refined on a CDC 74-16 computer by block-diagonal least squares (Cruickshank, 1961). For the H atoms, which were fixed at 1.08 Å from their respective C atoms, only the isotropic temperature factors were refined. For H, the f curve calculated by Stewart, Davidson & Simpson (1965) was used, for the other atoms the scattering factors of Doyle & Turner (1968). During the refinement we noted that $|F_o - F_c|$ was large for many low-order reflexions. Further refinement was therefore limited to the 11750 reflexions with $\sin \theta/\lambda > 0.4 \text{ \AA}^{-1}$. $R_w = [\sum w_c (F_o - F_c)^2 / \sum w_c F_o^2]^{1/2}$ dropped to 0.069. As $\langle w_c (F_o - F_c)^2 \rangle$ appeared to depend systematically on $|F|$, and on $\sin \theta/\lambda$, we chose a weighting scheme $w = [w_c^{-1} + P^2 F_o^2]^{-1}$ with $P^2 = 0.00037$ making the variation of $\langle w(F_o - F_c)^2 \rangle$ as small as

Table 3. $\langle w|F_o - F_c|^2 \rangle$ as a function of $|F|$ and $\sin \theta/\lambda$

$w = [w_c^{-1} + 0.00037|F_o|^2]^{-1}$. Nr: number of reflexions in a group. $w(F_o - F_c)^2$ is averaged over all reflexions of a group.

Nr	F_o limits	$\langle w(F_o - F_c)^2 \rangle$	Nr	$\sin \theta/\lambda$ limits	$\langle w(F_o - F_c)^2 \rangle$
947	0.0- 2.2	0.160	794	0.400-0.450	1.477
891	2.2- 3.0	0.251	991	0.450-0.500	1.161
724	3.0- 3.5	0.404	546	0.500-0.525	1.070
700	3.5- 4.0	0.603	597	0.525-0.550	0.788
770	4.0- 4.5	0.860	646	0.550-0.575	0.712
725	4.5- 5.0	0.928	668	0.575-0.600	0.709
689	5.0- 5.5	1.203	740	0.600-0.625	0.693
681	5.5- 6.0	1.114	760	0.625-0.650	0.632
654	6.0- 6.6	1.175	808	0.650-0.675	0.756
701	6.6- 7.3	1.119	880	0.675-0.700	0.702
749	7.3- 8.3	0.927	956	0.700-0.725	0.748
754	8.3- 9.5	0.916	917	0.725-0.750	0.778
672	9.5-11.0	1.097	1044	0.750-0.775	0.730
623	11.0-13.0	0.955	1026	0.775-0.800	0.831
1217	13.0-25.0	1.096	377	> 0.800	0.762
253	> 25.0	0.911			

possible. The values obtained for $\langle w(F_o - F_c)^2 \rangle$ at this stage of the refinement are given in Table 3.

One cycle of refinement with the new weighting scheme gave shifts in the parameters smaller than 2.5σ . During the following final cycle the shifts were smaller than 0.2σ . The final $R_w = [\sum w(F_o - F_c)^2 / \sum wF_o^2]^{1/2}$ was 0.107. The final parameters are listed in Tables 4 and 5 with their standard deviations calculated by the least-squares program.*

The difference map of the high-order reflexions did not reveal significant features. For the 1911 reflexions

with $\sin \theta/\lambda < 0.4 \text{ \AA}^{-1}$, a structure-factor calculation based on the final parameters gave $R = [\sum (F_o - F_c)^2 / \sum F_o^2]^{1/2} = 0.143$. The $(F_o - F_c)$ map of these reflexions showed a density cloud around the inversion centre $(0, \frac{1}{2}, 0)$ with a maximum of 1.2 e \AA^{-3} (14σ) and a smaller maximum ($0.6 \text{ e \AA}^{-3} = 7\sigma$) at $x = -0.02$, $y = 0.57$, $z = 0.49$.

Description of the structure

The individual molecules

There are two independent DPPH molecules in the unit cell, *A* and *B*. As can be seen from the stereoscopic picture (Fig. 1), the conformation of the two molecules is roughly the same and is moreover comparable with the DPPH conformation observed by Williams (1967) in DPPH-benzene. We could therefore apply Williams's numbering system (Fig. 2a).

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31692 (47 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 4. Final fractional atomic coordinates ($\times 10^5$)

Standard deviations are given in parentheses, in units of the last decimal place. The positions of the hydrogen atoms were not refined. The numbers of the hydrogen atoms correspond to those of the carbon atoms to which they are linked.

	Molecule A			Molecule B		
	x	y	z	x	y	z
C(1)	17893 (16)	8877 (13)	70222 (30)	15816 (20)	64905 (18)	67266 (41)
C(2)	15227 (17)	12546 (14)	53858 (31)	21944 (19)	67414 (16)	84967 (38)
C(3)	5219 (18)	13125 (15)	45292 (33)	18699 (20)	71945 (15)	97185 (36)
C(4)	-2532 (17)	9825 (14)	52387 (32)	8910 (20)	73738 (16)	92627 (37)
C(5)	-646 (16)	5892 (14)	67806 (31)	2120 (21)	71120 (19)	76282 (44)
C(6)	9347 (17)	5633 (13)	76312 (30)	5786 (22)	67036 (23)	63950 (46)
C(7)	33560 (17)	19954 (13)	83675 (32)	33738 (19)	67741 (15)	53481 (34)
C(8)	39416 (19)	24948 (15)	75851 (36)	44080 (20)	68076 (17)	61434 (39)
C(9)	37413 (23)	31922 (16)	76339 (44)	50084 (24)	74527 (20)	63458 (44)
C(10)	29689 (24)	34019 (17)	84579 (47)	45776 (30)	80572 (20)	57539 (54)
C(11)	24018 (23)	29035 (17)	92738 (45)	35445 (31)	80276 (19)	49919 (50)
C(12)	25967 (19)	22046 (15)	92513 (35)	29329 (24)	73831 (18)	47758 (40)
C(13)	44746 (17)	10279 (14)	84194 (32)	30585 (22)	54959 (16)	43415 (38)
C(14)	45616 (19)	3860 (15)	74855 (38)	26044 (29)	48437 (20)	47236 (51)
C(15)	55203 (22)	1578 (17)	76798 (47)	28565 (33)	42301 (20)	39176 (64)
C(16)	63688 (20)	5521 (19)	87842 (49)	35506 (34)	42671 (24)	27658 (61)
C(17)	62682 (20)	11763 (18)	97326 (43)	40025 (32)	49265 (24)	24059 (53)
C(18)	53170 (18)	14254 (15)	95398 (35)	37627 (25)	55497 (19)	31958 (41)
N(19)	27174 (14)	7590 (12)	80049 (28)	17988 (19)	60638 (17)	53655 (38)
N(20)	34919 (14)	12639 (12)	82014 (27)	27597 (17)	61151 (14)	51186 (33)
N(21)	22933 (16)	15483 (14)	44098 (28)	31616 (18)	64729 (15)	92129 (33)
O(22)	30413 (15)	12319 (14)	44273 (27)	32792 (20)	58752 (14)	87044 (32)
O(23)	21314 (17)	20895 (14)	35963 (30)	38031 (17)	68608 (14)	103694 (34)
N(24)	-13056 (16)	10564 (13)	43671 (30)	5666 (20)	78758 (14)	105270 (35)
O(25)	-14640 (16)	15191 (14)	32632 (31)	11798 (22)	81136 (16)	119330 (35)
O(26)	-19743 (14)	6538 (12)	47896 (32)	-3083 (18)	80404 (15)	100716 (39)
N(27)	11290 (15)	2026 (12)	93675 (28)	-806 (27)	65431 (23)	45135 (59)
O(28)	7963 (16)	-4239 (11)	92914 (29)	-9065 (27)	62634 (33)	44151 (64)
O(29)	15751 (14)	5465 (12)	107975 (25)	2350 (32)	67262 (28)	31390 (52)
H(3)	3528	16124	33209	23731	74051	110069
H(5)	-6758	3146	72930	5654	72281	73432
H(8)	45430	23375	69514	47378	63372	65960
H(9)	41878	35778	70268	58074	74854	69621
H(10)	28092	39452	84660	50508	85538	58881
H(11)	18084	30648	99236	32170	85011	45685
H(12)	21716	18215	99077	21323	73536	41792
H(14)	39030	768	66370	20685	48180	56241
H(15)	56058	-3321	69642	25137	37231	41900
H(16)	71068	3709	89019	37420	37884	21458
H(17)	69252	14727	106231	45399	49490	15099
H(18)	52363	19189	102482	41081	60584	29339

In Table 6 his values of bond lengths and angles are compared with our results. A number of approximately planar units can be distinguished in the DPPH

molecules (Fig. 2*b*). The equations of the least-squares planes and the deviations of the atoms from these planes are given in Table 7.

Table 5. *Final thermal parameters*

Temperature factors defined as: $\exp(-2\pi^2 \sum_{i,j} h_i h_j a_i^* a_j^* U_{ij})$. All values are multiplied by 10^4 and standard deviations are given in parentheses.

Molecule A						
	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(1)	125 (8)	209 (10)	145 (8)	12 (7)	20 (7)	10 (7)
C(2)	149 (9)	283 (12)	134 (8)	18 (8)	33 (7)	9 (8)
C(3)	171 (9)	311 (12)	150 (9)	32 (8)	24 (7)	15 (8)
C(4)	127 (8)	271 (11)	170 (9)	42 (8)	2 (7)	-35 (8)
C(5)	101 (8)	252 (11)	163 (9)	22 (7)	7 (7)	-15 (8)
C(6)	142 (8)	220 (10)	139 (8)	24 (7)	6 (7)	14 (7)
C(7)	137 (8)	219 (10)	153 (9)	0 (7)	26 (7)	2 (8)
C(8)	190 (10)	278 (12)	218 (10)	19 (9)	80 (8)	49 (9)
C(9)	278 (12)	254 (13)	344 (13)	14 (10)	114 (10)	68 (10)
C(10)	281 (12)	267 (13)	373 (14)	31 (10)	83 (11)	5 (11)
C(11)	254 (12)	304 (14)	350 (14)	11 (10)	137 (10)	-71 (11)
C(12)	181 (10)	304 (13)	194 (10)	-37 (9)	77 (8)	-33 (9)
C(13)	123 (8)	270 (11)	168 (9)	15 (8)	21 (7)	56 (8)
C(14)	169 (9)	278 (12)	253 (11)	33 (9)	47 (8)	26 (9)
C(15)	233 (11)	273 (13)	390 (14)	53 (10)	37 (10)	49 (11)
C(16)	153 (10)	395 (16)	421 (15)	78 (10)	57 (10)	167 (12)
C(17)	143 (10)	375 (15)	320 (13)	-3 (9)	-15 (9)	113 (11)
C(18)	147 (9)	301 (12)	199 (10)	-11 (8)	-10 (7)	47 (9)
N(19)	100 (7)	248 (10)	170 (8)	12 (6)	10 (6)	28 (7)
N(20)	116 (7)	235 (9)	139 (7)	-5 (6)	20 (6)	14 (7)
N(21)	175 (8)	377 (12)	120 (8)	-2 (8)	22 (6)	31 (8)
O(22)	167 (8)	487 (12)	180 (8)	11 (8)	50 (6)	3 (8)
O(23)	272 (10)	429 (12)	228 (9)	1 (8)	48 (7)	135 (8)
N(24)	141 (8)	279 (10)	199 (9)	58 (7)	-14 (7)	-19 (8)
O(25)	215 (8)	403 (11)	269 (9)	115 (8)	-5 (7)	90 (8)
O(26)	133 (7)	332 (10)	350 (10)	4 (7)	-5 (7)	6 (8)
N(27)	117 (7)	256 (10)	169 (8)	11 (7)	28 (6)	30 (7)
O(28)	253 (8)	229 (9)	264 (9)	4 (7)	49 (7)	49 (7)
O(29)	195 (8)	343 (10)	147 (7)	-13 (7)	-2 (6)	21 (7)
Molecule B						
	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(1)	167 (10)	390 (15)	273 (12)	-37 (10)	61 (9)	-50 (10)
C(2)	183 (10)	291 (13)	258 (11)	-6 (9)	69 (8)	55 (9)
C(3)	233 (11)	278 (12)	200 (10)	6 (9)	61 (8)	39 (9)
C(4)	213 (10)	290 (12)	238 (11)	-0 (9)	107 (8)	27 (9)
C(5)	162 (10)	430 (16)	315 (13)	-19 (10)	71 (9)	-28 (11)
C(6)	156 (11)	634 (22)	304 (14)	-30 (12)	16 (10)	-115 (14)
C(7)	207 (10)	280 (12)	184 (9)	36 (9)	74 (8)	11 (8)
C(8)	197 (10)	361 (14)	247 (11)	16 (10)	78 (9)	44 (10)
C(9)	274 (13)	444 (17)	294 (13)	-87 (12)	145 (10)	-31 (12)
C(10)	462 (18)	355 (16)	436 (17)	-60 (13)	324 (15)	-54 (13)
C(11)	534 (19)	335 (15)	370 (15)	133 (14)	304 (15)	91 (12)
C(12)	323 (13)	376 (15)	236 (11)	140 (11)	154 (10)	66 (10)
C(13)	272 (12)	281 (13)	226 (11)	53 (10)	17 (9)	-10 (9)
C(14)	376 (15)	332 (16)	367 (15)	-27 (12)	15 (12)	-31 (12)
C(15)	451 (19)	297 (16)	521 (20)	26 (14)	-77 (15)	-42 (14)
C(16)	470 (19)	427 (19)	452 (19)	216 (16)	-147 (15)	-136 (15)
C(17)	443 (18)	511 (21)	362 (16)	256 (16)	72 (13)	-50 (14)
C(18)	334 (14)	399 (16)	229 (12)	124 (12)	51 (10)	-4 (11)
N(19)	191 (9)	435 (15)	298 (11)	-47 (9)	71 (8)	-83 (10)
N(20)	180 (9)	312 (11)	242 (10)	7 (8)	62 (7)	-12 (8)
N(21)	221 (10)	345 (12)	222 (9)	39 (9)	58 (8)	53 (9)
O(22)	411 (12)	341 (11)	282 (10)	105 (9)	103 (9)	36 (8)
O(23)	221 (9)	391 (12)	339 (10)	7 (8)	15 (8)	27 (9)
N(24)	281 (11)	279 (11)	271 (10)	67 (9)	108 (8)	54 (9)
O(25)	419 (13)	491 (14)	289 (10)	197 (11)	6 (9)	-37 (10)
O(26)	239 (9)	396 (12)	467 (13)	86 (9)	111 (9)	23 (10)
N(27)	336 (15)	553 (20)	534 (19)	60 (14)	18 (13)	-92 (16)
O(28)	317 (14)	117 (36)	633 (21)	0 (17)	-99 (13)	-196 (22)
O(29)	550 (20)	879 (27)	429 (16)	-13 (18)	41 (14)	27 (16)

Table 6. Bond lengths (Å) and angles (°)

Values for DPPH-C₆H₆ were taken from Williams (1967). The standard deviations in the bond lengths and angles as obtained from the standard deviations in the coordinates (Table 4) vary from 0.003 to 0.006 Å and from 0.2 to 0.4° respectively.

	<i>A</i>	<i>B</i>	DPPH-C ₆ H ₆		<i>A</i>	<i>B</i>	DPPH-C ₆ H ₆
C(1)—C(2)	1.425	1.426	1.420	C(1)—C(2)—C(3)	122.7	122.5	123.1
C(2)—C(3)	1.392	1.385	1.366	C(2)—C(3)—C(4)	119.3	118.7	119.2
C(3)—C(4)	1.381	1.383	1.389	C(3)—C(4)—C(5)	122.0	122.8	121.2
C(4)—C(5)	1.388	1.393	1.384	C(4)—C(5)—C(6)	117.1	116.9	117.8
C(5)—C(6)	1.378	1.369	1.370	C(5)—C(6)—C(1)	125.5	124.7	124.7
C(6)—C(1)	1.426	1.436	1.412	C(6)—C(1)—C(2)	113.4	114.1	113.9
C(7)—C(8)	1.404	1.399	1.373	C(7)—C(8)—C(9)	119.4	119.4	119.9
C(8)—C(9)	1.386	1.393	1.380	C(8)—C(9)—C(10)	120.8	120.0	120.7
C(9)—C(10)	1.397	1.393	1.370	C(9)—C(10)—C(11)	119.5	120.7	119.7
C(10)—C(11)	1.402	1.393	1.378	C(10)—C(11)—C(12)	120.6	120.0	120.9
C(11)—C(12)	1.387	1.396	1.382	C(11)—C(12)—C(7)	119.4	119.1	118.6
C(12)—C(7)	1.407	1.400	1.405	C(12)—C(7)—C(8)	120.4	120.8	120.2
C(13)—C(14)	1.402	1.402	1.369	C(13)—C(14)—C(15)	118.3	118.6	119.7
C(14)—C(15)	1.395	1.392	1.383	C(14)—C(15)—C(16)	121.0	120.4	120.9
C(15)—C(16)	1.390	1.390	1.375	C(15)—C(16)—C(17)	120.1	120.1	119.4
C(16)—C(17)	1.385	1.406	1.379	C(16)—C(17)—C(18)	120.2	120.7	120.9
C(17)—C(18)	1.403	1.397	1.403	C(17)—C(18)—C(13)	119.1	117.8	117.9
C(18)—C(13)	1.394	1.400	1.393	C(18)—C(13)—C(14)	121.3	122.4	121.2
C(1)—N(19)	1.369	1.358	1.370	C(2)—C(1)—N(19)	130.6	129.5	130.6
N(19)—N(20)	1.334	1.349	1.334	C(6)—C(1)—N(19)	115.8	116.4	115.3
N(20)—C(7)	1.429	1.422	1.422	C(1)—N(19)—N(20)	118.4	118.3	118.5
N(20)—C(13)	1.430	1.419	1.419	N(19)—N(20)—C(7)	121.9	121.7	121.8
C(2)—N(21)	1.472	1.463	1.463	N(19)—N(20)—C(13)	115.8	115.6	115.1
N(21)—O(22)	1.229	1.218	1.232	C(7)—N(20)—C(13)	122.1	122.1	122.0
N(21)—O(23)	1.235	1.239	1.216	N(20)—C(7)—C(8)	120.4	119.6	121.5
C(4)—N(24)	1.464	1.465	1.452	N(20)—C(7)—C(12)	119.2	119.6	118.3
N(24)—O(25)	1.235	1.222	1.236	N(20)—C(13)—C(14)	118.2	117.7	119.5
N(24)—O(26)	1.231	1.241	1.217	N(20)—C(13)—C(18)	120.5	120.0	119.3
C(6)—N(27)	1.474	1.486	1.471	C(1)—C(2)—N(21)	121.5	121.6	121.1
N(27)—O(28)	1.230	1.180	1.205	C(3)—C(2)—N(21)	115.6	115.6	115.3
N(27)—O(29)	1.222	1.231	1.217	C(2)—N(21)—O(22)	117.8	118.8	118.5

Table 6 (cont.)

	<i>A</i>	<i>B</i>	DPPH-C ₆ H ₆
C(2)—N(21)—O(23)	117.4	117.5	117.2
O(22)—N(21)—O(23)	124.7	123.7	124.2
C(3)—C(4)—N(24)	119.4	118.4	119.7
C(5)—C(4)—N(24)	118.6	118.8	119.1
C(24)—N(24)—O(25)	118.0	118.0	117.4
C(4)—N(24)—O(26)	117.6	117.3	118.1
O(25)—N(24)—O(26)	124.4	124.7	124.5
C(5)—C(6)—N(27)	117.0	116.5	116.6
C(1)—C(6)—N(27)	117.5	118.5	118.7
C(6)—N(27)—O(28)	117.2	117.5	117.1
C(6)—N(27)—O(29)	118.4	119.5	117.7
O(28)—N(27)—O(29)	124.3	122.9	125.1

Apart from the presence of NO₂ groups and a central N—N bond instead of a C—N double bond, DPPH is similar to *N*-(diphenylmethylene)aniline, sometimes referred to as TPI. The conformations of our *A* and *B*, Williams's DPPH molecule and the TPI molecule (Tucker, Hoekstra, ten Cate & Vos, 1975) are compared in Table 8, which lists values of some short intramolecular distances and some angles between planar units. In the discussion below, DPPH will be compared with TPI and with parts of tetraphenylhydrazine (TPH) (Hoekstra, Vos, Braun & Hornstra, 1975). Average values of corresponding bond lengths and angles in the three DPPH molecules will be used, unless stated otherwise.

The central skeleton

The value of the central N—N bond in *A*, 1.334 (3), is slightly smaller than that in *B*, 1.349 (4), and equal to that in DPPH—benzene, 1.334 (6) Å. As to a good approximation, the N atoms of the N—N bonds in DPPH, TPH (Fig. 3) and hexanitroazobenzene (HNAB) have the same *sp*² hybridization, the N—N bond in DPPH can be compared with the single N—N bond in TPH, 1.41 Å [π bond order 0.02; Hoekstra & Vos (1975)] and the double N—N bond in HNAB, 1.24 Å (Graeber & Morosin, 1975). The comparison shows that the N—N bond in DPPH is considerably shorter than the N—N single bond and considerably longer than the N—N double bond. This agrees with the fact that in addition to the σ bond, the N—N bond in the DPPH radical has a π bond with two electrons in a bonding and one electron in an antibonding π orbital.

The DPPH molecules are far from planar, as is shown by the large values of dihedral angles in Table 8. The torsion angle of the N—N bond is 30°. This is smaller than the torsion of the N—N single bond in TPH (74°), but larger than that of the C—N double bond in TPI (7.6°) and the N—N double bond in HNAB (0 and 2.5°). These values, though undoubtedly influenced by steric effects, indicate also that the N—N bond in DPPH lies between a single and a double bond. The angle between planes IV and II [mainly a torsion

around N(20)–C(7)] is 37, 42 and 49° for *A*, *B* and DPPH–benzene respectively. For the angle between IV and III [torsion around N(20)–C(13)] these values are 31, 27 and 22°.

The differences between corresponding torsion angles in the three molecules can also be noticed from the variations in corresponding intramolecular distances, e.g. for C(1)---C(12), C(7)---C(8) and N(19)---C(14) (Table 8). It is noticeable that the sum of the torsion angles around the bonds between N(20) and the two phenyl groups linked to it is approximately the same (69°) for the three DPPH molecules. This is also the case for the three independent pairs of N–(Ph)₂ torsion angles in TPH (49°). In TPI one pair of N–(Ph)₂ torsion angles is present with a sum of 77°. The increasing value of the sum when going from TPH *via* DPPH to TPI is due to the decreasing value for the angle C–N–C in the same direction (Fig. 3) due to which the centres of neighbouring phenyl rings come closer together.

The differences between the angles C–N–C mentioned above follow from a consideration of the approximately planar central skeletons of TPH, DPPH and TPI given in Fig. 3. For skeletons of this type the angles around each atom of the central bond are determined mainly by the repulsion between the atoms linked to it (Hoekstra & Vos, 1975; see also Gillespie, 1972; Bartell, 1960). Due to this, in TPH all three distances in the triangle around the central N

atom are approximately equally shorter than the sum of the relevant van der Waals radii (1.7 for C, 1.5 Å for N). In DPPH and TPI an extra distortion occurs

Table 8. Angles (°) between some planar units (see Fig. 2b), and short intramolecular distances (Å) in DPPH and TPI molecules

For definitions of planes see Table 7.

Angle	<i>A</i>	<i>B</i>	DPPH–C ₆ H ₆	TPI
I–IV	57.8	54.8	55.4	67.8
II–IV	36.9	42.4	48.5	48.3
III–IV	31.1	27.1	21.7	29.3
V–IV	31.0	31.3	28.5	7.6
I–V	34.5	31.6	33.0	63.4
VI–I	35.6	32.4	24.8	–
VII–I	15.1	5.5	13.4	–
VIII–I	60.6	57.1	54.5	–
Distance				
N(19)–C(13)	2.34	2.34	2.31	2.38
N(19)–C(7)	2.42	2.42	2.41	2.47
N(19)–C(14)	2.76	2.73	2.70	2.84
N(19)–C(12)	2.90	2.92	2.92	3.10
N(20)–C(1)	2.32	2.32	2.31	2.35
N(20)–C(2)	3.02	2.98	3.01	3.05
C(13)–C(7)	2.50	2.49	2.48	2.54
C(7)–C(1)	2.83	2.84	2.83	2.88
C(7)–C(18)	2.95	2.91	2.86	2.96
C(13)–C(8)	3.02	3.03	3.08	3.05
C(1)–C(12)	2.92	3.01	3.05	3.05
C(18)–C(8)	3.11	3.09	3.09	3.16
C(7)–C(2)	3.12	3.08	3.11	3.20

Table 7. Least-squares planes and distances of atoms to these planes

For numbering of planes see also Fig. 2(b).

(a) Equations of least-squares planes $lX + mY + nZ = P$

X, Y, Z in a right-handed orthogonal coordinate system with $X \parallel a^*$ and $Z \parallel c$. *X, Y, Z* and *P* are in Å.

Plane	Atoms included	Molecule <i>A</i>			Molecule <i>B</i>				
		<i>l</i>	<i>m</i>	<i>n</i>	<i>l</i>	<i>m</i>	<i>n</i>	<i>P</i>	
I	C(1), C(2), C(3), C(4), C(5), C(6)	–0.0049	0.8325	0.5540	3.7081	0.3207	0.7714	–0.5497	7.8816
II	C(7), C(8), C(9), C(10), C(11), C(12)	0.6857	0.1142	0.7437	7.0540	–0.1864	0.1979	–0.9623	3.8925
III	C(13), C(14), C(15), C(16), C(17), C(18)	–0.1543	–0.4790	0.8642	2.6658	0.7450	–0.1214	–0.6560	2.9831
IV	C(7), C(13), N(19), N(20)	0.0936	–0.0214	0.9954	5.3441	0.3662	–0.2621	–0.8929	0.4857
V	C(11), N(19), N(20)	–0.2231	0.3955	0.8909	4.1261	0.2116	–0.7230	0.6576	–5.7821
VI	N(21), O(22), O(23)	0.4873	0.5064	0.7114	4.5475	–0.4049	–0.3142	0.8587	–0.8854
VII	N(24), O(25), O(26)	–0.0452	0.6613	0.7488	4.1467	–0.3294	0.6224	–0.7100	–6.5953
VIII	N(27), O(28), O(29)	–0.8704	0.3615	0.3343	0.9781	0.3302	–0.1316	–0.9347	–12.0719

(b) Distances to least-squares planes in 10^{–3} Å

For each plane are consecutively given: atom, distance for molecule *A*, and distance for molecule *B*.

Plane I	Plane II	Plane III	Plane IV	Plane V	Plane VI	Plane VII	Plane VIII
C(1) 11 18	C(7) –15 –7	C(13) –5 –3	C(15) –1 3	C(1) 0 0	N(21) 0 0	N(24) 0 0	N(27) 0 0
C(2) –18 –32	C(8) 6 3	C(14) 7 2	C(16) –8 –1	N(19) 0 0	O(22) 0 0	O(25) 0 0	O(28) 0 0
C(3) 7 14	C(9) 6 4	C(1) 11 18	C(17) 11 0	N(20) 0 0	O(23) 0 0	O(26) 0 0	O(29) 0 0
C(4) 11 18	C(10) –9 –9	C(2) 6 13	C(18) –4 2	C(7) 680 –716	C(2) –37 68	C(4) 6 –33	C(6) 62 –63
C(5) –17 –31	C(11) 0 5	N(19) –49 –19	N(19) –658 –704	C(13) –608 577			
C(6) 6 13	C(12) 12 2	N(20) –185 –284	N(20) –11 –54				
N(19) –49 –19	N(19) –806 –662	N(24) 69 121					
N(21) –185 –284	N(20) –130 –22	N(27) 106 227	Plane IV	Plane VI	Plane VIII		
N(24) 69 121			C(7) 11 17	N(21) 0 0	N(27) 0 0		
N(27) 106 227			C(13) –32 –51	O(22) 0 0	O(28) 0 0		
			N(19) 11 16	O(23) 0 0	O(29) 0 0		
			N(20) 10 16	C(2) –37 68	C(6) 62 –63		
			C(1) –586 –569				

around the central N atom, caused by the short distance (strong repulsion) between C(1) and C(7). Due to the increase in the angle C(7)N(20)N(19), the picryl group is bent away from the C(7)C(12) phenyl ring (plane II). It is interesting to note that all non-bonded distances given for DPPH in Fig. 3 are 0.05 Å shorter than the corresponding distances in TPI.

The picryl group

The distance of the picryl group from plane II is enlarged by the increase of the angle C(7)N(20)N(19) (see above) and moreover by the widening of the angle N(19)C(1)C(2) to as much as 130°. Partly as a consequence of this, the angles C(2)C(1)C(6), 114°, and N(19)C(1)C(6), 116°, are small. As has been discussed by Domenicano, Vaciago & Coulson (1975), substitution of a benzene H atom by an NO₂ group increases the adjacent CCC angle to 122°. In 2,4,6-trinitrobenzene, where the CCC angles have alternating values of 124 and 116°, this effect turns out to be even stronger (Choi & Abel, 1972). Considerations like these may also partly explain the small value of the angle C(2)C(1)C(6).

In the picryl group considerable torsions are present around the C–NO₂ bonds, evidently to avoid large intramolecular repulsions. It should be noticed, however, that the values of the dihedral angles between the NO₂ groups and the phenyl ring (twist angles) are also influenced by the crystal packing, because twist angles observed for nitrobenzenes and for the *para*-NO₂ groups in compounds like DPPH vary from 0 to 28°. The *para*-twist angle in DPPH, which has different values between 5 and 15° for the three molecules, is smaller than the *ortho*-twist angles, approximately 31° for plane VI and 57° for VIII. The twist angle of plane VI is considerably smaller than the twist angle of VIII because the distance of VI from the central skeleton is already enlarged by the bending of the angle

N(19)C(1)C(2). This effect is also present in serotonin picrate (Thewalt & Bugg, 1972).

C(1)–C(2) and C(1)–C(6) are relatively long (1.42 Å). A similar elongation is present in picrates (Maartmann-Moe, 1969) and in HNAB, and is caused by steric hindrance between the *ortho*-NO₂ groups and the central skeleton. Short distances such as O(22)---

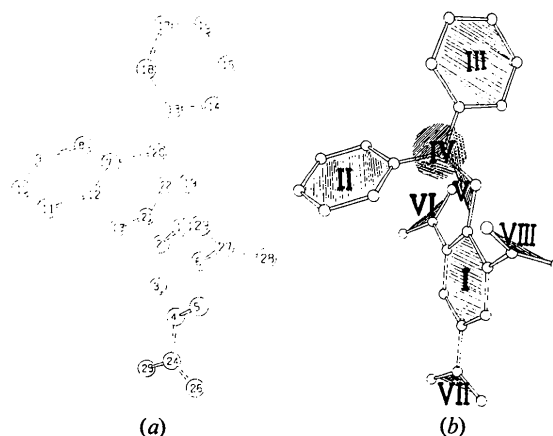


Fig. 2. (a) Atomic numbering in DPPH. (b) Numbering of planes.

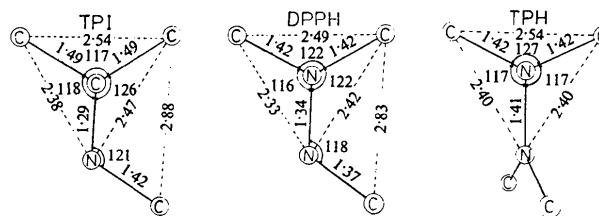


Fig. 3. Distances (Å) and angles (°) in the central skeletons of TPH, DPPH and TPI. The torsion around the central N–N bond is 74° in TPH and 30° in DPPH. In TPI the torsion is 7.6° around the central C=N bond.

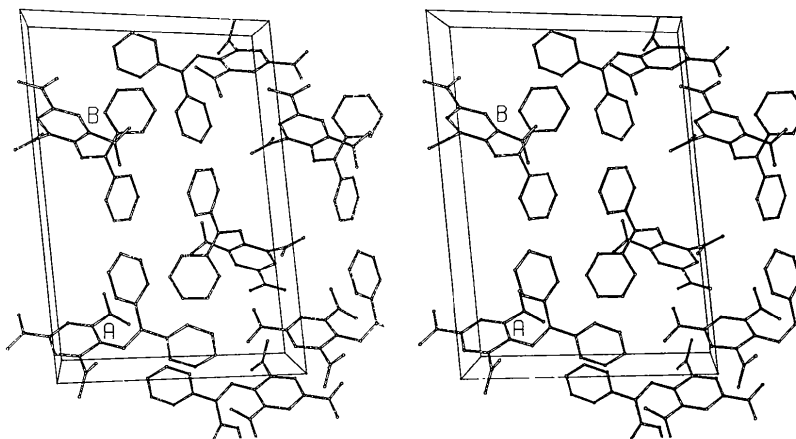


Fig. 1. Stereoscopic packing diagram of DPPH-IIIa. Drawing made by ORTEP-II (Johnson, 1971). View is down *c* with *a* approximately horizontal.

N(20), 2.70, and O(29)---N(19), 2.81 Å, probably play an important role in these effects.

N-C bonds

Different values for N-C bonds have been observed, between the values for a single bond, 1.472 (5) Å for a three-covalent N (Sutton, 1965), and a double bond, 1.286 Å in TPI. In DPPH various kinds of N-C bonds are present. The C-NO₂ lengths, 1.466, 1.460 and 1.477 Å for C(2)-N(21), C(4)-N(24) and C(6)-N(27) respectively, are close to the C-N single-bond value, the adjacent CCC angles being 122.8, 122.3 and 124.9° respectively. The variations indicate that a smaller bond length corresponds to a smaller bond angle as has also been shown by Choi & Abel (1972). Correlations between N-C and N-O lengths in nitro groups and the O-N-O angle have been discussed, among others, by Williams (1967).

The average value found for the N(20)-C(phenyl) bonds, 1.424 Å, is approximately equal to the N-C(phenyl) lengths observed in TPH and TPI (1.42 Å). N(19)-C(1) has a still smaller value (1.37 Å). Gubanov, Pereliaeva, Chirkov & Matevosian (1970) have calculated bond orders for DPPH [0.436 for N-N, 0.369 for N-C(phenyl) and 0.513 for N-C(picryl)], but they assume that the molecule is planar and that N(19) has *sp* hybridization. Their results are therefore not applicable to the DPPH molecules in the crystals, where smaller bond orders are expected due to the non-planarity of the molecules and *sp*² hybridization at N(19).

Crystal packing and thermal motion

In the structure a channel with a diameter at least 6 Å is present around the line $[0, \frac{1}{2}, z]$. In the final low-order difference map we observed maxima in this area (see *Refinement*). In view of the composition found for DPPH-IIIa (Table 1) it seems likely that solvent molecules are present here. From the magnitude of the density cloud (diameter 3.5 to 4.0 Å) we think an acetone molecule is accommodated around the inversion centre $(0, \frac{1}{2}, 0)$, where the channel has a diameter of approximately 8 Å. Acetone molecules do not contain an inversion centre and are probably randomly distributed in the holes. The possibility that in some cases alkanes (from petroleum spirit 60-80°) or more acetone molecules are present in the channels cannot be excluded with certainty but this would result in structural distortions.

An analysis of the thermal parameters (Cruickshank, 1956) showed that the DPPH molecules are not rigid bodies. The thermal motion of *A* is considerably smaller than that of *B* (Table 5). The average *u*² values for the atoms of the phenyl rings of *A* are 0.019, 0.025 and 0.026 Å² for C(1)C(6), C(7)C(12) and C(13)C(18) respectively. In *B* these values are 0.028, 0.032 and 0.039 Å². This phenomenon can be explained by the fact that the *B* molecules surround the channels mentioned above, so

that these molecules have a relatively large freedom of motion. A slight disordering of the *B* molecules cannot be excluded either. Especially for the nitro group N(27)O(28)O(29) in *B*, which sticks into the channel, large thermal parameters are observed, while N(27)-O(28) is very short (1.18 Å). The nitro group has short distances to the small maximum observed in the low-order difference map [for O(28) 1.59 Å, for N(27) 1.73 Å], so that the anomalies of N(27)O(28)O(29) are probably an artefact caused by possible disorder and the presence of solvent molecules.

Physical properties

The DPPH molecule contains one unpaired electron giving rise to interesting magnetic properties. Gubanov, Koriakov, Chirkov & Matevosian (1970) have calculated spin densities in DPPH both for *sp*² and *sp* hybridization of N(19). In both cases approximately 60% of the spin density is located on the central N atoms. The calculations were done, however, on a planar model of the molecule. Several authors (Gubanov, Koriakov & Chirkov, 1973; Dalal, Kennedy & McDowell, 1973) conclude from EPR and ENDOR experiments that in solution DPPH has *sp* hybridization, with equal unpaired electron-spin distributions for the two phenyl groups. This is clearly not true for the molecular structures observed in

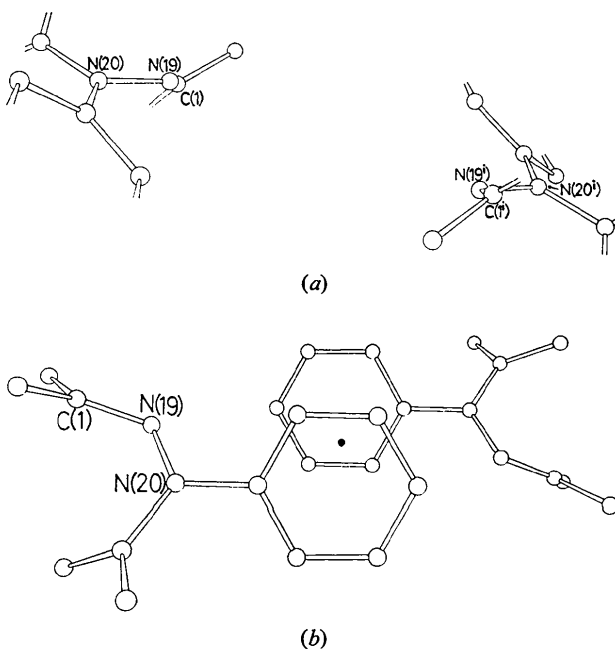


Fig. 4. Possible interactions between adjacent radicals. (a) Parts of two *B* molecules around the inversion centre $(0, \frac{1}{2}, z)$. N(19)---N(19^b) = 5.95 Å. The perpendicular distance between the two parallel planes C(1)N(19)N(20) is 1.98 Å. (b) Parts of two *A* molecules around the inversion centre $(\frac{1}{2}, 0, 1)$. N(20)---N(20^b) = 6.92 Å. N(19)---N(19^b) = 7.23 Å. The perpendicular distance between the two parallel C(13)C(18) phenyl groups is 3.93 Å.

DPPH-benzene and DPPH-IIIa. NMR measurements by Yoshioka, Ohya-Nishiguchi & Deguchi (1974) show indeed considerable differences between spectra of DPPH in solution and of crystals of DPPH-benzene. Moreover, they find that the unpaired electron-spin delocalization is larger in the crystalline state than in solution.

Susceptibility measurements as a function of temperature were made by Duffy & Strandburg (1967) on DPPH-I and -II. Earlier measurements by Duffy (1962) on DPPH, crystallized from carbon disulphide, and by van Isterbeek & Labro (1964) on a modification crystallized from chloroform, probably refer to DPPH-III, but melting points of their materials were not reported. Fedders & Kommandeur (1970) explain the magnetic properties of DPPH by the narrow-band model, which has been worked out for a one-dimensional spin system. In their opinion, bandwidths and gaps are small for small electron overlap between neighbouring radicals in both the two- and the three-dimensional case. From the magnetic data of Duffy & Strandburg (1967), Fedders & Kommandeur have calculated small bandwidths and gaps for DPPH-I and -II. They presume that the difference between the two modifications is due to differences between the, as yet unknown, crystal structures. Our crystal structure indicates that for DPPH-IIIa the overlap between adjacent radicals is small, as large intermolecular distances are found between the central N atoms which we assume to have a relatively high unpaired electron-spin density. The shortest N...N distance is 5.95 Å, and is found between N(19) in *B* and N(19¹) in *B*¹ related to *B* by the inversion centre at (0, $\frac{1}{2}$, $\frac{1}{2}$); *B* and *B*¹ are separated by the channel mentioned above (Fig. 4a). For *A* the shortest N...N distance, 6.92 Å, is found between N(20) of *A* and the atom related to it by the inversion centre at ($\frac{1}{2}$, 0, 1). The two atoms are separated, however, by two parallel C(13)C(18) phenyl groups, which lie at a perpendicular distance of 3.93 Å from each other (Fig. 4b).

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