

Structural Studies of 2,2-Diphenyl-1-picrylhydrazine: A Clathrate Forming Compound

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Abstract. 2,2-Diphenyl-1-picrylhydrazine was crystallized from both tetrahydrofuran and chloroform. The crystal structures of samples from both preparations were determined by X-ray diffraction at low temperatures. Both crystals are clathrates with solvent molecules included as guest species in a host framework formed by the diphenylpicrylhydrazine molecules. The structures are rhombohedral, space group $R\bar{3}$. For the crystal from tetrahydrofuran, at 228 K, $a = 25.820(4)$, $c = 15.096(2)$ Å, $Z = 18$, $R = 0.084$ and $wR = 0.133$. For the crystal from chloroform, at 115 K, $a = 25.453(12)$, $c = 15.083(3)$ Å, $Z = 18$, $R = 0.117$ and $wR = 0.153$. Each unit cell contains three cavities which have approximate cylindrical shape with diameter 7.8 Å and height 6.0 Å, and $\bar{3}$ point symmetry. The integrity of the host framework is maintained only through van der Waals forces rather than through intermolecular hydrogen bonding as is found in many other known organic clathrates. The conformation of the trinitroanilino group of the hydrazine molecule is similar to that in the related trinitroanilino carbazole molecule. The N—N bond approximates a single bond, and both hydrazine N atoms are sp^2 hybridized.

Key words. Diarylpicrylhydrazine, clathrate, single crystal, crystal structure.

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1. Introduction

Diarylpicrylhydrazines and related hydrazyls are able to crystallize from many organic solvents and adopt several crystalline forms, most of which include solvent molecules [1–6]. The only reported crystal structures of hydrazine compounds are for 9-(2,4,6-trinitroanilino)carbazole [7] and 2,4,6-trinitrophenylhydrazine [8]. The structure of potassium 1-(*N,N*-diphenylhydrazono)-2,4,6-trinitrobenzenide has also been reported [9]. As a part of an investigation of the structural properties of a series of picrylhydrazine derivatives, we report here the structure of 2,2-diphenyl-1-picrylhydrazine which forms a clathrate with its solvent. Cell constant data have been reported previously [10].

Typical organic clathrates can accommodate guest molecules ranging widely in size and shape without changing the structure of the host framework [11–13]. There are usually no strong interactions between the host framework and the guest molecules. In most known organic clathrate crystals, the framework of the host

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molecules involves intermolecular hydrogen bonds [11]. They usually exhibit three-fold symmetry such as in the space groups $P3$, $P\bar{3}$, $R3$ and $R\bar{3}$ [11], with the cavities located at special positions in the unit cell. Typical guest solvent molecules do not have the high symmetry of the cavity. The number of guest molecules in each cavity may not be constant for a given crystal sample, and the average occupancy of the cavities may vary between samples. Molecules in partially-filled cavities may be quite mobile, or may undergo enhanced thermal motion. The electron density of the guest molecules is averaged by the diffraction experiment, both over time and over all the cavities in the sample. Therefore, it may represent highly disordered molecular positions [14, 15].

The 2,2-diphenyl-1-picrylhydrazine molecule is closely related to the stable organic free radical 2,2-diphenyl-1-picrylhydrazyl, important in electron paramagnetic resonance spectroscopy and as an H-atom abstractor. This hydrazyl molecule has been studied in several different crystalline forms, some of which contain solvent molecules but none of which contains clathrate cavities [1, 5].

Studies of 2,2-diphenyl-1-picrylhydrazine in liquid solution using variable temperature ^1H and ^{13}C NMR spectroscopy [6, 16, 17] have revealed that the chemical shifts of the two picryl protons *meta* to the N—N linkage are quite different at low temperature. With increasing temperature, the separated peaks corresponding to the two *meta* protons in the spectra merge into a single peak. It was assumed that the high-temperature equivalence of the two protons results from the environments of the two protons interchanging through an internal reorientation process. It was proposed [16] that a major contribution to the energy associated with the reorientation process is the one associated with the breakage of an intramolecular hydrogen bond between the hydrazine hydrogen atom and an oxygen atom of a nitro group *ortho* to the N—N linkage.

Studies have been carried out to clarify the involvement of the intramolecular hydrogen bond in the reorientation process [16, 17]. Based on a lineshape analysis of the NMR spectra of diphenylpicrylhydrazine in a variety of perdeuterated solvents with different hydrogen-bond (proton-accepting) ability, it was concluded that the internal reorientation process indeed involves the breakage of the intramolecular hydrogen bond. However, other factors, such as the partial double-bond character and steric repulsions within the hydrazine molecules [7] also contribute to the height of the reorientation barrier.

2. Experimental

2,2-Diphenyl-1-picrylhydrazine was synthesized by the method reported by Weil, Sane and Kinkade [18]. Two crystals, $D(t)$ and $D(c)$, of 2,2-diphenyl-1-picrylhydrazine were obtained from tetrahydrofuran and from chloroform, respectively. The three-fold rotational symmetry of both crystals was established from the X-ray diffraction patterns on precession photographs and confirmed by Weissenberg photographs. The extinction condition ($-h + k + l = 3n$) indicated a rhombohedral lattice. There was no evidence of any other symmetry elements. The possible space groups of the crystals are therefore limited to $R\bar{3}$ or $R3$. The approximate unit cell parameters of the crystals were determined from precession photographs.

Table I. Experimental data for unit-cell parameter refinements and intensity data collections

Crystals	<i>D</i> (t)	<i>D</i> (c)
formula	C ₁₈ H ₁₃ N ₅ O ₆	C ₁₈ H ₁₃ N ₅ O ₆
molar mass (g/mol)	395.33	395.33
solvent	tetrahydrofuran	chloroform
color	red	red
crystal system	rhombohedral	rhombohedral
space group	$R\bar{3}$	$R\bar{3}$
<i>a</i> (Å)	25.820(4)	25.453(12)
<i>c</i> (Å)	15.096(2)	15.083(12)
<i>V</i> (Å ³)	8716(2)	8463(5)
<i>Z</i>	18	18
ρ_{calc} (g/cm ³) ^a	1.397	1.468
number of reflections used for unit cell parameter refinement	30	32
λ : MoK α (Å)	0.70926	0.70926
2 θ range (deg) for cell parameter refinement	40.0–43.0	40.0–43.0
temperature (K)	228	115
μ (cm ⁻¹) ^a	1.16	1.89

^aThe values were calculated assuming one guest molecule per cavity and the cell volumes as measured at 228 and 115 K, respectively.

The measurements of the intensities and the determinations of accurate unit cell parameters were carried out on a modified Picker FACS-I four-circle diffractometer controlled by a PDP8a/OS computer with the NRCC diffractometer control program [19]. The MoK α X-ray beam was monochromated by a graphite crystal with 0.7 perfection factor. An Enraf-Nonius universal low-temperature device was used for cooling the specimen. The unit-cell parameters and other crystal data for both crystals are listed in Table I. During the intensity data collection, three reference reflections were measured after every 47 reflections. The decrease in the intensities of the reference reflections caused by crystal decay was insignificant. Only one independent set of reflection data was collected for each crystal.

The intensities of reflections were corrected for Lorentz and polarization effects. The variances of the intensities were estimated from counting statistics and from the machine instability factor. For the reflections with $I \leq 3\sigma(I)$, the Bayesian statistical method was applied to estimate the correct structure factors and standard deviations. The statistics of the normalized structure factors of the crystals clearly showed a centrosymmetric crystal structure, which suggested that the space group of both crystals is $R\bar{3}$.

The structures of both crystals were independently solved by direct methods and Fourier synthesis. The non-hydrogen atoms of the hydrazine molecule were located on the best Fourier *E*-map. After the positions of all the non-hydrogen atoms of the hydrazine molecule were located and refined, the positions of the hydrogen atoms were either located from a difference Fourier synthesis or calculated, based on known structural parameters. The structures were refined by full-matrix least-

squares methods with anisotropic temperature factors for non-hydrogen atoms, and isotropic temperature factors for hydrogen atoms. Reflections with $I \geq 2\sigma(I)$ were used for the structure refinements. The intensity data reduction, structure determinations and structure refinements used the XTAL system of crystallographic programs [20].

After the least-squares refinements of the structures had converged, with all atoms of the diphenylpicrylhydrazine molecules included, the molecular packing diagrams showed large cavities in both crystalline forms. Within the cavities, several prominent electron density peaks were found on the difference Fourier maps. The electron densities associated with the peaks in the $D(c)$ crystal were substantially larger than those in the $D(t)$ crystal. Two significant independent peaks were found in the cavity for the $D(t)$ crystal. Three peaks were found for the $D(c)$ crystal, the two larger of which had approximately the same electron density as a host carbon atom. The two peaks in the $D(t)$ structure had coordinates nearly identical to the two larger peaks in the $D(c)$ structure but their heights were roughly 1/3 those of host carbon atoms. The electron density of the third peak in the $D(c)$ structure was also 1/3 that of a host carbon atom.

In an attempt to confirm the presence of guest solvent molecules in the crystals, the densities of the crystals were carefully measured by the flotation method in zinc iodide aqueous solutions at room temperature. Accurate unit cell constants and cell volumes were initially measured for both samples at the same reduced temperatures at which the diffraction intensities were measured, rather than at room temperature. To investigate the temperature dependence of the cell constants and cell volumes, and to calculate the cell volumes at room temperature, the thermal expansion coefficients of the unit-cell parameters were determined [21] using the relations

$$a(T) = a_0(1 + \alpha_a T) \quad \text{and} \quad c(T) = c_0(1 + \alpha_c T), \quad (1)$$

where a_0 and c_0 are the values of the cell parameters at 0 K, and α_a and α_c are the thermal expansion coefficients of the unit cell parameters. A crystal of $D(c)$ was used to measure the crystal unit cell parameters at 171, 198, 246 and 292 K, using the diffractometer. The 0 K parameters for the crystal are $a_0 = 25.21(2)$ Å, and $c_0 = 15.06(1)$ Å, and the expansion coefficients are $\alpha_a = 95(4) \times 10^{-6} \text{ K}^{-1}$ and $\alpha_c = 7(4) \times 10^{-6} \text{ K}^{-1}$. It was assumed that the thermal expansion coefficients were not affected by the nature of the guest molecules. Therefore, the thermal expansion coefficients for the $D(t)$ crystal were assumed to be the same as those for the $D(c)$ crystal, and a_0 and c_0 were calculated from the single measurement of the unit-cell parameters at 228 K, yielding $a_0 = 25.27(2)$ (Å), and $c_0 = 15.07(1)$ Å.

The average number, N_s , of solvent molecules in the unit cell of a crystal, based on the measured density, can then be calculated from

$$N_s = \frac{D_{\text{obs}} VA - ZM(\text{host molecule})}{M(\text{solvent molecule})}, \quad (2)$$

where the unit-cell volume V of the crystals is based on the unit-cell parameters calculated at room temperature from the thermal-expansion coefficients, A is Avogadro's number, M is the molecular mass and Z is the number (18) of host

Table II. Density, D_{obs} , of diphenylpicrylhydrazine crystals at 297 K

Solvent	D_{obs} (g/cm ³)	cell volume (Å ³)	N_c ^a
tetrahydrofuran	1.40(1)	8820(15)	4.5(8)
chloroform	1.46(1)	8773(15)	5.0(4)

^a N_c is the calculated average number of guest molecules per unit cell.

molecules in the unit cell. Each unit cell contains 3 cavities. The results, given in Table II, clearly indicate that the solvent molecules are cocrystallized with diphenylpicrylhydrazine molecules. However, the average number of solvent molecules in the cavity is not an integer.

High-resolution proton NMR spectra of $D(t)$ and $D(c)$ in deuterated solvents were also measured. The spectra showed that the tetrahydrofuran molecules are co-crystallized with diphenylpicrylhydrazine molecules in the crystals of $D(t)$. However, the spectra of several $D(c)$ crystals were measured and gave results which were inconsistent: some spectra showed evidence for the presence of chloroform molecules but some did not. The quantitative analysis of the spectra suggested that the $D(t)$ crystal contained 9 solvent molecules in the unit cell whereas some $D(c)$ crystals contained approximately 5 solvent molecules in the unit cell and others contained none.

For both $D(t)$ and $D(c)$ crystals, the electron density peaks in the Fourier map of the cavity, which are assumed to be contributed from the solvent molecules, were taken into consideration in the final refinements. In the $D(t)$ crystal, an oxygen atom with population parameter 1/3 was assigned to the highest peak in the cavity and a carbon atom with population parameter 1/3 was assigned to the next highest peak in the cavity. In the $D(c)$ crystal, two chlorine atoms with 1/3 population parameters were assigned to the two highest peaks in the cavity and one carbon atom with population parameter 1/3 was assigned to the next-highest peak. The results of refinements with and without the presence of the guest atoms are given in Table III. Inclusion of the guest atoms substantially improves the overall agreement factors, R and wR . The differences in the molecular structure of the host molecules from refinements including and excluding the guest atoms are insignificant.

Table III. Results of refinements of the $D(t)$ and $D(c)$ crystal structures

	$D(t)$	$D(t)$ ^a	$D(c)$	$D(c)$ ^a
R	0.200	0.084	0.247	0.117
wR	0.265	0.133	0.358	0.153
number of least-squares variables	314	322	314	341
number of reflections used in the refinement	2477	2477	2718	2718
scale factor	1.1981	1.0124	1.0398	0.8404

^a The guest atoms are included.

3. Results and Discussion

3.1. MOLECULAR STRUCTURE

The coordinates and equivalent isotropic temperature factors for the non-hydrogen atoms and H(7) for the $D(c)$ crystals are listed in Table IV with estimated standard deviations given in parentheses. The bond lengths, bond angles and other structural parameters for $D(t)$ and $D(c)$ are given in Table V, with estimated standard

Table IV. Atom coordinates and temperature factors for 2,2-diphenyl-1-picrylhydrazine (chloroform), $D(c)$

Atom	x/a	y/b	z/c	$U_{eq} (\text{\AA}^2)$
H(7)	-0.054(3)	0.786(3)	0.085(4)	4(2)
C(1)	0.0220(2)	0.7864(2)	0.1134(3)	2.7(2)
C(2)	0.0227(2)	0.7866(2)	0.2080(3)	3.1(2)
C(3)	0.0663(3)	0.7822(2)	0.2552(4)	3.5(3)
C(4)	0.1102(3)	0.7777(2)	0.2119(4)	3.6(3)
C(5)	0.1152(3)	0.7793(2)	0.1200(3)	3.2(2)
C(6)	0.0706(2)	0.7844(2)	0.0746(3)	2.7(2)
C(11)	-0.0643(2)	0.7061(3)	-0.0383(3)	3.2(2)
C(12)	-0.0994(3)	0.6661(3)	0.0273(4)	4.1(3)
C(13)	-0.1319(3)	0.6042(3)	0.0121(5)	5.1(4)
C(14)	-0.1279(3)	0.5815(3)	-0.0708(5)	5.6(4)
C(15)	-0.0905(3)	0.6221(3)	-0.1360(5)	5.1(4)
C(16)	-0.0580(3)	0.6835(3)	-0.1202(4)	4.1(3)
C(21)	-0.0295(5)	0.8149(2)	-0.0810(3)	2.9(2)
C(22)	-0.0620(2)	0.7989(3)	-0.1601(3)	2.9(2)
C(23)	-0.0559(2)	0.8440(3)	-0.2181(3)	3.1(2)
C(24)	-0.0193(3)	0.9042(3)	-0.1968(4)	3.7(3)
C(25)	0.0110(3)	0.9200(3)	-0.1161(4)	3.7(3)
C(26)	0.0059(2)	0.8754(2)	-0.0586(3)	2.9(2)
N(2)	-0.0221(2)	0.7923(2)	0.2589(3)	3.9(2)
N(4)	0.1569(3)	0.7716(2)	0.2628(3)	4.2(3)
N(6)	0.0818(2)	0.7920(2)	-0.0230(3)	3.2(2)
N(7)	-0.0226(2)	0.7869(2)	0.0664(3)	3.0(2)
N(8)	-0.0304(2)	0.7701(2)	-0.0230(2)	2.6(2)
O(21)	-0.0196(2)	0.7915(2)	0.3406(2)	4.9(2)
O(22)	-0.0615(2)	0.7985(2)	0.2202(3)	4.8(2)
O(41)	0.1976(2)	0.7706(2)	0.2235(3)	5.4(2)
O(42)	0.1503(2)	0.7689(2)	0.3447(3)	5.6(2)
O(61)	0.0978(2)	0.8423(2)	-0.0534(2)	3.6(2)
O(62)	0.0788(2)	0.7498(2)	-0.0650(3)	4.8(2)
C(14)	0.1279(3)	0.5815(3)	-0.0708(5)	5.6(4)
C(15)	-0.0905(3)	0.6221(3)	-0.1360(5)	5.1(4)
C(16)	-0.0580(3)	0.6835(3)	-0.1202(4)	4.1(3)
C(21)	-0.0295(2)	0.8149(2)	-0.0810(3)	2.5(2)
C(22)	-0.0620(2)	0.7989(3)	-0.1601(3)	2.9(2)
C(23)	-0.0559(2)	0.8440(3)	-0.2181(3)	3.1(2)
C(24)	-0.0193(3)	0.9042(3)	-0.1968(4)	3.7(3)
C(25)	0.0110(3)	0.9200(3)	-0.1161(4)	3.7(3)
C(26)	0.0059(2)	0.8754(2)	-0.0586(3)	2.9(2)

deviations based on the variances and covariances of the atom parameters. A stereoscopic view and atom numbering scheme for the molecules are given in Figures 1 and 2, respectively.

The structure of the trinitroanilino group in the 2,2-diphenyl-1-picrylhydrazine molecule is very similar to that in the 9-(2,4,6-trinitroanilino)carbazole molecule [7]. An O atom (O(22)) of a nitro group *ortho* to the hydrazine linkage forms an intra-molecular hydrogen bond with the hydrazine H atom. The distance N(7)⋯O(22) in the diphenylpicrylhydrazine molecule (2.600(6) Å for *D*(t) and 2.596(6) Å for *D*(c)) is substantially shorter than the normal value (2.90 Å) for a hydrogen bond [22] because the angle (N—H⋯O) in the hydrazine molecule is much less than 180°. Due to the presence of the intramolecular hydrogen bond, the

Table V. Bond lengths (Å) and bond angles (°) in 2,2-diphenyl-1-picrylhydrazine

	<i>D</i> (t)	<i>D</i> (c)		<i>D</i> (t)	<i>D</i> (c)
C(1)—C(2)	1.403(6)	1.426(7)	C(11)—C(8)—C(21)	123.9(4)	124.7(4)
C(1)—C(6)	1.430(7)	1.392(7)	C(1)—N(7)—N(8)	120.9(4)	119.7(4)
C(2)—C(3)	1.381(7)	1.368(8)	C(11)—N(8)—N(7)	115.2(4)	114.7(4)
C(3)—C(4)	1.364(8)	1.348(9)	C(21)—N(8)—N(7)	113.9(4)	113.7(4)
C(4)—C(5)	1.389(7)	1.391(7)	C(2)—N(2)—O(21)	118.0(5)	118.7(5)
C(5)—C(6)	1.375(7)	1.386(7)	C(2)—N(2)—O(22)	118.8(4)	119.7(4)
C(11)—C(12)	1.398(8)	1.381(8)	C(4)—N(4)—O(41)	118.1(5)	119.2(5)
C(11)—C(16)	1.387(7)	1.405(8)	C(4)—N(4)—O(42)	116.7(6)	115.1(6)
C(12)—C(13)	1.392(9)	1.385(9)	C(6)—N(6)—O(61)	117.0(4)	116.6(4)
C(13)—C(14)	1.35(1)	1.40(1)	C(6)—N(6)—O(62)	117.4(5)	118.3(4)
C(14)—C(15)	1.39(1)	1.40(1)	O(21)—N(2)—O(22)	123.1(5)	121.7(5)
C(15)—C(16)	1.395(9)	1.376(9)	O(41)—N(4)—O(42)	125.2(5)	125.7(5)
C(21)—C(22)	1.382(7)	1.391(7)	O(61)—N(6)—O(62)	125.3(5)	124.9(4)
C(21)—C(26)	1.383(7)	1.383(7)	N(2)—O(21)	1.225(5)	1.235(5)
C(22)—C(23)	1.369(7)	1.389(8)	N(2)—O(22)	1.220(6)	1.235(6)
C(23)—C(24)	1.378(8)	1.376(8)	N(4)—O(41)	1.232(7)	1.203(7)
C(24)—C(25)	1.385(8)	1.390(8)	N(4)—O(42)	1.231(6)	1.243(7)
C(25)—C(26)	1.372(8)	1.382(8)	N(6)—O(61)	1.223(5)	1.222(6)
C(1)—N(7)	1.355(6)	1.348(7)	N(6)—O(62)	1.221(6)	1.216(6)
C(11)—N(8)	1.444(6)	1.429(7)	C(1)—C(1)—C(6)	114.4(4)	114.2(5)
C(21)—N(8)	1.437(6)	1.428(6)	C(1)—C(2)—C(3)	122.8(5)	122.0(5)
C(2)—N(2)	1.475(7)	1.444(7)	C(2)—C(3)—C(4)	119.8(5)	119.6(5)
C(6)—N(6)	1.484(6)	1.496(6)	C(3)—C(4)—C(5)	121.4(5)	123.2(5)
C(4)—N(4)	1.467(7)	1.488(7)	C(4)—C(5)—C(6)	117.8(5)	115.4(5)
N(7)—N(8)	1.381(5)	1.400(5)	C(1)—C(6)—C(5)	123.7(4)	125.4(5)
C(2)—C(1)—N(7)	123.7(5)	122.4(5)	C(12)—C(11)—C(16)	120.0(5)	119.5(6)
C(6)—C(1)—N(7)	121.9(4)	123.3(4)	C(11)—C(12)—C(13)	120.3(6)	121.2(6)
C(12)—C(11)—N(8)	120.5(5)	121.6(5)	C(12)—C(13)—C(14)	119.7(7)	119.4(7)
C(16)—C(11)—N(8)	119.4(5)	118.7(5)	C(13)—C(14)—C(15)	120.8(7)	119.1(7)
C(22)—C(21)—N(8)	122.3(4)	121.4(5)	C(14)—C(15)—C(16)	120.5(7)	121.2(6)
C(26)—C(21)—N(8)	119.1(4)	118.7(4)	C(11)—C(16)—C(15)	118.6(7)	119.3(6)
C(1)—C(2)—N(2)	121.1(5)	121.5(5)	C(22)—C(21)—C(26)	118.6(5)	119.8(5)
C(3)—C(2)—N(2)	116.1(5)	116.5(5)	C(21)—C(22)—C(23)	120.5(5)	119.6(5)
C(5)—C(4)—N(4)	118.9(5)	116.9(5)	C(22)—C(23)—C(24)	120.7(5)	120.5(5)
C(3)—C(4)—N(4)	119.6(5)	119.9(5)	C(23)—C(24)—C(25)	119.2(6)	119.6(5)
C(1)—C(6)—N(6)	121.7(4)	121.7(4)	C(24)—C(25)—C(26)	119.8(6)	120.2(5)
C(5)—C(6)—N(6)	114.3(4)	112.8(5)	C(21)—C(26)—C(25)	121.1(6)	120.1(5)

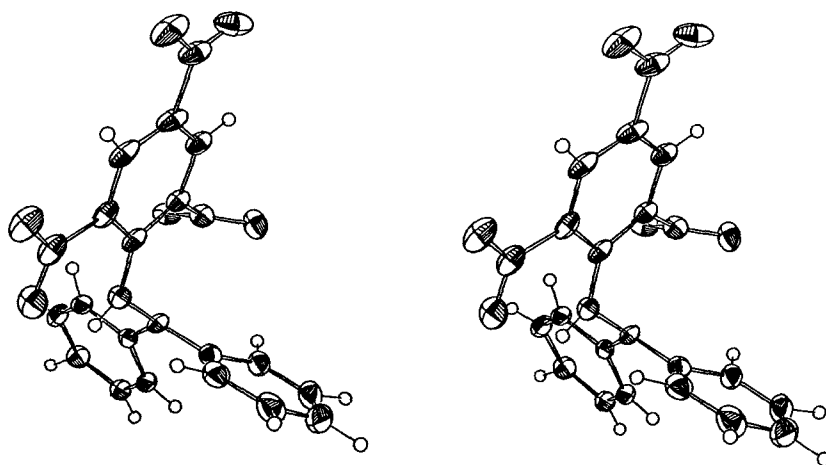


Fig. 1. Stereoscopic view of the 2,2-diphenyl-1-picrylhydrazine molecule.

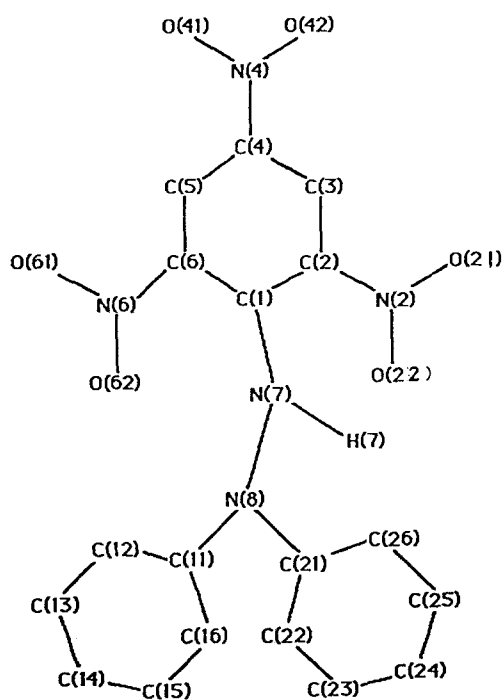


Fig. 2. Atom-numbering scheme of the 2,2-diphenyl-1-picrylhydrazine molecule.

Table VI. Dihedral angles ($^{\circ}$) between planes, least-squares fitted to positions of atoms, as defined in Figure 4, in 2,2-diphenyl-1-picrylhydrazine

Plane 1	Plane 2	$D(t)$	$D(c)$
A	B	2.2(7)	3.0(6)
A	C	2.7(5)	2.4(2)
A	D	68.4(2)	68.7(2)
A	F	89.6(2)	90.1(2)
A	G	94.6(2)	93.5(2)
E ^a	F	42.5(2)	33.0(2)
E	G	14.8(2)	18.1(2)
F	G	47.9(2)	46.2(2)

^aPlane least-squares fitted to positions of atoms N(7), N(8), C(11) and C(21).

hydrogen-bonded *ortho*-nitro group is forced to be coplanar with the phenyl plane of the picryl group. The other *ortho*-nitro group is twisted away from coplanarity with the phenyl plane due to steric hindrance from the phenyl groups at the other end of the hydrazine linkage. There are no unusually short intermolecular contact distances in the crystal structures, and neighboring molecules would not be expected to have a significant effect on the conformation of a molecule. The *para*-nitro group is almost coplanar with the phenyl plane. The dihedral angles between the nitro planes and the phenyl plane of the picryl group for both crystalline forms are listed in Table VI.

In both diphenylpicrylhydrazine crystal structures, the length of the C(1)—N(7) bond is close to that of the C—N partial double bond in the related hydrazyl (1.352 Å) [5] and in trinitroanilino-carbazole (1.355(4) and 1.361(4) Å) [7]. Due to the intramolecular hydrogen bond, the plane of the σ -bond system¹ of the N(7) atom is forced to be coplanar with the phenyl plane of the picryl group. This brings one of the N(7) *p* orbitals (containing lone-pair electrons) perpendicular to the phenyl plane of the picryl group. The lone-pair electrons of the N(7) atom then can participate in the picryl π -electron system to the maximum extent possible. In contrast, the plane of the σ -bond system of the N(7) atom in the diphenylpicrylhydrazyl free radical [5] and in the related hydrazinate [9] is twisted away from coplanarity with the picryl plane.

The N(8) atom is also sp^2 hybridized (with some sp^3 character). The arrangement of atoms linked to the hydrazine group shows a staggered conformation, which minimizes the steric interactions between the picryl group at one end of the hydrazine linkage and the aromatic groups at the other. The torsional angles around the hydrazine linkage are shown in Figure 3. For $D(c)$, the values of α_1 , α_2 , α_3 , α_4 , C(2)—C(1)—N(7)—H(7) and C(6)—C(1)—N(7)—N(8) are 125.0(5), 82.6(6), 80(4), 73(4), 5(6) and 17.5(4) $^{\circ}$, respectively. The angle between the planes C(1)—N(7)—H(7) and C(11)—N(8)—C(21) is 91(6) $^{\circ}$.

Both the N(7) and N(8) atoms in these molecules are sp^2 hybridized, and the N—N bond is essentially a single bond with some π -bonding character, with bond

¹ The plane of the σ -bond system is the plane fitted by least squares to the central atom and the three atoms connected to it by σ bonds.

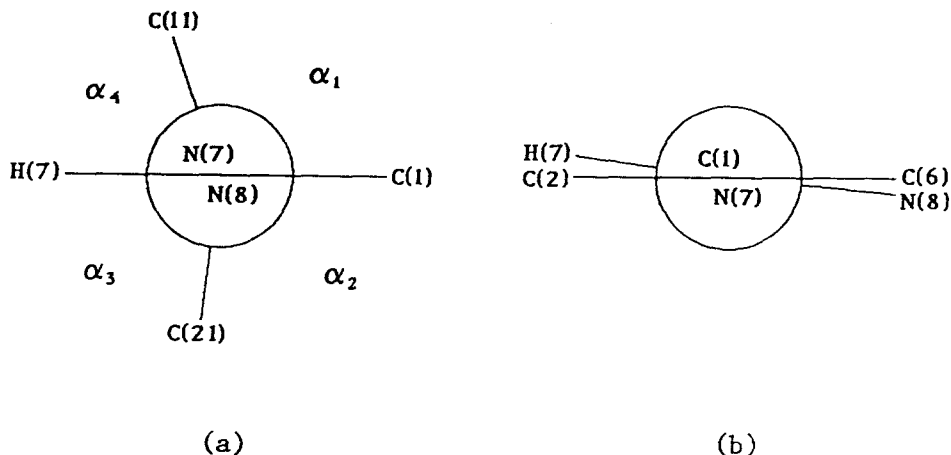


Fig. 3. Newman projection along: (a) the N—N bond, (b) the C(1)—N(7) bond. The values of the angles, α , are given in the text.

lengths 1.400(5) and 1.381(5) Å in *D(c)* and *D(t)*, respectively. The π -bonding is limited by the large dihedral angles between the planes of the two nitrogen σ -bond systems. The N—N single bond length in the hydrazine molecule is 1.449(4) Å [23] and 1.451(3) Å in dimethyldi(diphenylphosphino)hydrazine [24]. The N—N double bond length in the 2,2',4,4',6,6'-hexanitroazobenzene molecule is 1.24 Å [25].

The distortion of the phenyl ring of the picryl group from full hexagonal symmetry, as manifested by the deviation of its endocyclic angles from 120°, is consistent in magnitude and direction with that expected for the substituents present [26]. The increased endocyclic angles at the C(2), C(4) and C(6) atoms (Table V) are induced by the electron-withdrawing properties of the nitro groups, caused by an increase in the *p* character of the carbon σ -bonding orbital pointing towards the nitro group and a consequent decrease in the *p* character of the other two σ -bonding orbitals. Due to these enlarged endocyclic angles, the endocyclic angles at the C(2), C(4) and C(6) atoms are decreased, to maintain planarity of the phenyl ring. A substantial decrease in the endocyclic angle at C(1) arises from the electron-donating property of the amide group. Furthermore, the endocyclic angles at atoms C(2), C(4) and C(6) show a correlation with the dihedral angles of the nitro groups with respect to the phenyl plane. As the dihedral angle increases, the resonance interaction of the nitro group with the phenyl ring is decreased and the *p* character of the σ -bonding orbital (which points towards the nitro group) of the substituted carbon is reduced, leading to a smaller endocyclic angle at that carbon atom on the phenyl ring.

3.2. MOLECULAR PACKING

The crystal structure of 2,2-diphenyl-1-picrylhydrazine has revealed the presence of large cavities in the crystal. The centers of the cavities are located at 0,0,1/2 and equivalent sites of the unit cell. These sites have $\bar{3}$ symmetry. The unique axis of

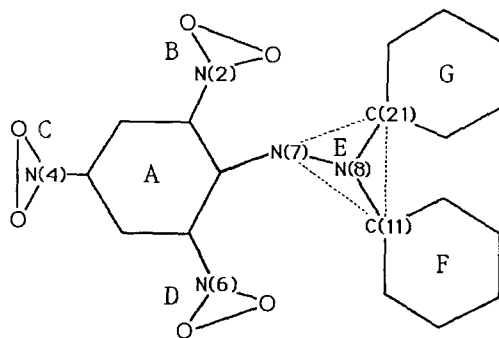


Fig. 4. Designation of planes in 2,2-diphenyl-1-picrylhydrazine.

a site is parallel to the c axis of the unit cell, as defined in terms of a hexagonal coordinate system (see Figure 4).

Several schematic diagrams of the cavity of the crystals were prepared in order to study the size and the shape of the cavity. In order to generate Figure 5, the positions of those atoms whose surfaces form the wall of the cavity were first rotated onto the ac face of the unit cell by a rotation about the c axis. The line was then constructed from circles drawn about each atom, each circle having a radius equal to the van der Waals radius of that atom. Therefore the shape of the cavity shown in Figure 5 is that of the largest cylindrical object which can fit into the cavity. The diameter of the cavity is approximately 7.8 \AA and the height of the cavity is approximately 6.0 \AA . There is considerably more space available for shapes not constrained to purely cylindrical symmetry.

A narrow tunnel, with a diameter of approximately 1 \AA , connects the cavities along the c direction. Therefore, it is difficult for any organic solvent molecule to migrate from one cavity to the next. In effect, the cavities are completely enclosed by the host molecules. Figure 6 shows the cross-sections of the cavity at various levels along the c axis.

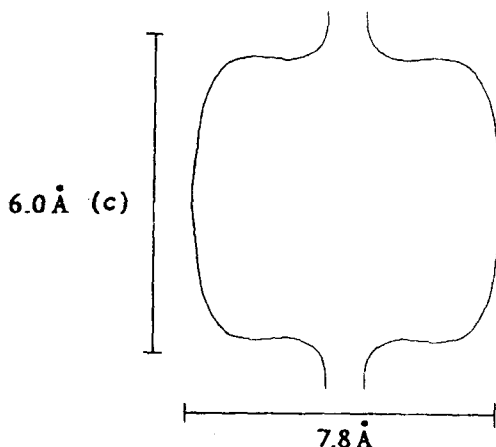


Fig. 5. Projection of the cylinder of rotation of the cavity.

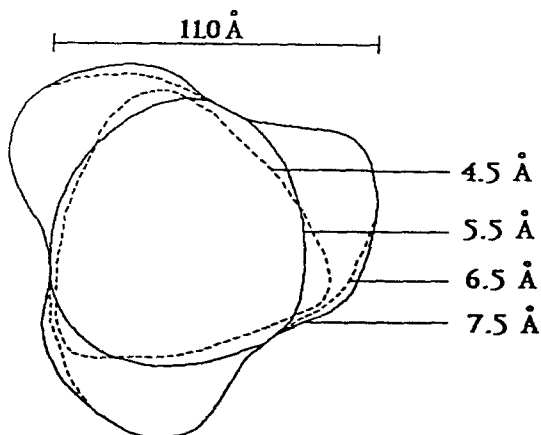


Fig. 6. Cross-sections of the cavity perpendicular to the c axis.

An independent set of the atoms making up the surface of the cavity is listed in Table VII, as are their distances (d) to the central c axis. These atoms belong to five different diphenylpicrylhydrazine molecules around a cavity: (i) C(5), C(6), N(6), O(61), O(62); (ii) C(23), H(23), H(24); (iii) C(14), H(13), H(14); (iv) C(3), H(3); and (v) O(41). A total of 30 molecules surround each cavity, of which six form the top of the cavity, six form the bottom and 18 form the sides. Therefore, each individual molecule only has a small contact area with any one cavity. The

Table VII. Coordinates of the atoms forming the surface of the cavity in $D(c)$ crystals

Atom	d^a	SO	x/a	y/b	z/c
C(6)	5.83(1)	2	0.2136	0.2363	0.2070
C(23)	3.55(1)	4	0.0566	0.1567	0.2158
O(62)	4.65(1)	2	0.2028	0.1416	0.2197
H(24)	1.5(4)	4	0.0170	0.0665	0.2286
C(5)	6.64(1)	2	0.2181	0.2838	0.2551
N(6)	5.11(1)	2	0.2082	0.1854	0.2589
H(23)	3.8(1)	4	0.0785	0.1676	0.2677
H(13)	5.7(2)	15	0.2512	0.0843	0.2681
O(61)	5.159(9)	2	0.2090	0.1891	0.3399
C(14)	6.00(3)	15	0.2514	0.0442	0.4020
H(3)	6.6(2)	11	0.2945	0.1841	0.4114
H(14)	5.0(2)	15	0.2059	0.0263	0.4129
O(41)	5.42(1)	16	0.1035	0.2414	0.4439
C(3)	7.56(2)	11	0.3325	0.2194	0.4536

^aDistance to the c axis.

Symmetry operators (SO):

2: $y, -x - y, z$

4: $-x, -y, -z$

11: $-x - y + 2/3, x + 1/3, z + 1/3$

15: $-y + 2/3, x + y + 1/3, -z + 1/3$

16: $-y + 1/3, x + y + 2/3, -z + 2/3$

molecules around the cavity are packed in such a way that only an edge of a phenyl or picryl group of a host molecule points toward the cavity. In contrast, the cavities in Dianin's compounds and in the quinol clathrates, which also have space group $R\bar{3}$ [11–15], are surrounded by only six molecules and the surface of the cavity is made up by the planes of the aromatic groups of the molecules.

A search of the literature shows that, in many known organic clathrates, intermolecular hydrogen bonds constitute the main forces which bind the host molecules together to form stable structures. In diphenylpicrylhydrazine crystals, there is no evidence of intermolecular hydrogen bonding, or of any conventional enhanced intermolecular interactions, such as charge transfer, between the host molecules.

MacNicol and coworkers [27, 28] have generated a series of compounds based on large hexa-substituted benzenes and octa-substituted naphthalenes that also form clathrates without the use of hydrogen bonds to maintain the host framework. In these compounds, the shape of the molecules is such that they cannot pack to completely fill space so that cavities are formed.

In sufficiently concentrated liquid solution, the molecular packing of the host molecules may involve the formation of a stable cluster of six molecules with approximate local $\bar{3}$ point symmetry. Crystallization then would involve cubic closest packing of the clusters. Because of the size of the clusters, the size of the inter-cluster gap is large enough to include solvent molecules. Each cavity is formed by eight clusters, with two of them covering the top and bottom openings of the cavity respectively.

Although the contacts between adjacent molecules within the cluster are not sufficiently short for them to be considered to be of the charge-transfer type, the arrangement, as shown in Figure 7, allows the electron-withdrawing picryl rings to be close to the electron-donating phenyl rings of an adjacent molecule in the cluster. Therefore, the formation of the clusters allows the dipolar 2,2-diphenyl-1-picrylhydrazine molecules to pack with their electric dipoles alternating in direction around the ring, staggered so that both poles in each dipole are adjacent to the opposite pole of a neighboring dipole. The packing contacts between adjacent molecules in Figure 7 are closely related to the π -molecular contact between adjacent molecules

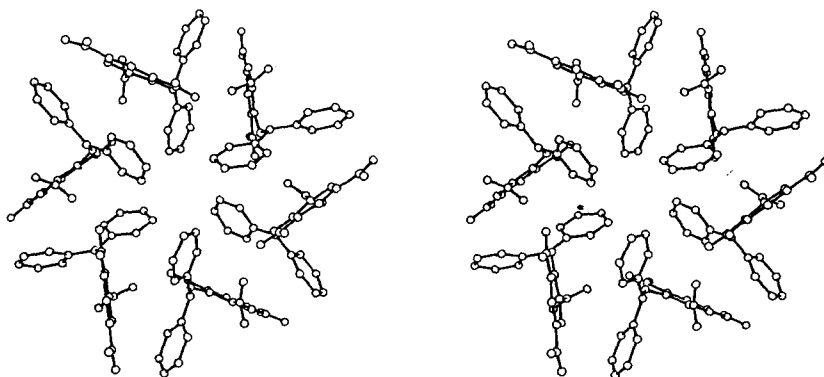


Fig. 7. Stereoscopic view of a cluster containing six diphenylpicrylhydrazine molecules.

in the related single-component π -molecular donor-acceptor compound 9-(2,4,6-trinitroanilino)carbazole [7].

The structures of the chloroform and tetrahydrofuran molecules are well known [29], and the approximate external dimensions of the molecules can be calculated. Based on the results of such calculations, it has not been possible to predict an arrangement of two or more (of either) guest molecules that would allow these to fit into the cavity, although neither molecule can fill the cavity completely. Furthermore, neither has $\bar{3}$ symmetry.

These observations, together with the results of attempts to measure directly the number of guest molecules by NMR and by density measurement, and the nature of the electron density of the guest molecules as observed by diffraction, clearly indicate that the positions, orientations and occupancies of the guest molecules are highly disordered, both in that they vary between cavities, and they may vary within one cavity over time. The guest molecule would be expected to be attracted to positions on the surface of the cavity where the van der Waals interactions between the host molecules and the guest molecules are optimized, generating the observed electron density peaks in the cavities.

The results do not exclude the possibility that the cavities may include other impurity molecules or air molecules.

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