the data reported by Pettersson and Lindholm do not seem to us to warrant this conclusion. Haynes and Kebarle[12] find that the propyl ions formed by the reaction of methane reactant ions with C_3D_8 comprise the ion $C_3D_7^+$ and $C_3D_6H^+$ in relative amounts of 20:1. Roughly half the propyl ions are formed by deuteride ion abstraction reactions with $C_2H_5^+$ from methane, and thus decomposition of the $C_3D_8H^+$ ion formed by proton transfer from CH_5^+ produced $C_3D_7^+$ and $C_3D_6H^+$ ions roughly in the ratio of 10:1. One concludes that the transferred proton does not become equivalent to the other hydrogens in the propane.[13] In our opinion, the weight of evidence so far available is that with the possible exception of methane and ethane, hydrogen molecules ejected from a protonated saturated hydrocarbon contain a large fraction of the hydrogen entity initially transferred to the hydrocarbon.

Analytical Considerations. We have pointed out above that the alkylcycloalkanes produce ions in both the $C_nH_{2n+1}^+$ and $C_nH_{2n-1}^+$ series. We showed earlier[3] that aliphatic hydrocarbons produce only $C_nH_{2n+1}^+$ ions, and thus in the analysis of a mixture of aliphatic and cycloalkanes some interference may be expected. Fortunately for almost all practical purposes the interference will be small and can be neglected or approximate corrections can be applied. While an inspection of Table I reveals that some cycloalkanes produce alkyl ions with appreciable intensities, these ions invariably contain only three to five carbon atoms. Since analyses using methane reactant chemical ionization mass spectrometry will surely be restricted to relatively large molecules, alkyl ions containing three to five carbon atoms will not constitute restrictive interferences. The average intensity for $C_nH_{2n+1}^+$ with $m/e > 85$ is 0.0089, which comprises contributions from $(MW + 1)^+$ ions (average intensity = 0.026 for alkylcyclopentanes other than cyclopentane and methylcyclopentane and average intensity = 0.011 for alkylcyclohexanes other than cyclohexane) and alkyl ions with $m/e < MW + 1$ (average intensity 0.009). Thus meaningful interferences would be encountered only in the unlikely case of an analysis of trace amounts of aliphatic paraffins in cycloparaffins.

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(13) Haynes and Kebarle[12] state the opposite conclusion, but Professor Kebarle has informed us that this statement constitutes an inadvertent error.

Crystal Structure of 2,2-Diphenyl-1-picrylhydrazyl Free Radical[1]

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Abstract: The crystal structure of the stable free radical 2,2-diphenyl-1-picrylhydrazyl (DPPH) has been determined from three-dimensional X-ray diffraction data. The molecular configuration around the second nitrogen is approximately trigonal planar with the phenyl groups twisted at angles of 49 and 22°. The bond at the digonal nitrogen is bent with a C–N–N angle of 118.5° and the attached picryl carbon is twisted 28.5° out of the plane of the trigonal hydrazine nitrogen. The nonplanarity of the hydrazyl backbone was not predicted from analyses of electron paramagnetic resonance measurements. The picryl ring plane is further inclined at an angle of 33° to the plane of the digonal nitrogen. The *o*-nitro groups are twisted out of the picryl ring plane by 25 and 55° while the *p*-nitro group is twisted by 13°. The stabilizing effect of the nitro groups on the radical is discussed. The hydrazyl N–N bond distance is 1.334 A, intermediate between expected values for single and double bonds. The benzene molecules of solvation are separated by normal van der Waals distances from the DPPH molecules; distances between DPPH molecules also are normal van der Waals contacts.

The stable free radical 2,2-diphenyl-1-picrylhydrazyl (DPPH) has been widely used as a homogeneous raddical detector[2a] and as a calibration standard for electron paramagnetic resonance (epr) spectrometers.[2b] The epr hyperfine splitting caused by the magnetic moments of the two hydrazyl nitrogen nuclei has been extensively studied and interpreted in terms of spin densities.[3] A very high resolution epr spectrum revealed additional hyperfine splittings which can be ascribed to the phenyl protons and/or nitro nitrogens.[4] Several proton magnetic resonance (pmr) investigations[5] have also shown the existence of spin density at the protons, and the Overhauser effect has been observed[6] with this substance.

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(1) This work was performed in the Ames Laboratory of the U. S. Atomic Energy Commission. Contribution No. 2047.

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At least three crystal forms of solvent-free DPPH[7] are known as well as numerous forms containing molecules of solvation. Good quality crystals may be readily prepared by crystallizing DPPH from benzene–hexane solution in which case a molecule of benzene is incorporated into the structure for each molecule of DPPH. Crystallographic data for DPPH–C_6H_6 have previously been reported by Sternberg.[8] A preliminary communication has been published[9] on the work fully reported here.

Collection and Treatment of X-Ray Data

Precession and Weissenberg X-ray diffraction photographs obtained from single crystals of DPPH–C_6H_6 mounted in thin-walled capillaries showed monoclinic symmetry. Reflections in the ($h0l$) zone were observed only when $l = 2n$, indicating the space groups P2/c or Pc. Since the crystals are observed to be piezoelectric,[8] the indicated space group is Pc. Using chromium Kα radiation, 14 reflection angles in the back reflection region were accurately determined with a single-crystal orienter diffractometer equipped with a scintillation counter detector. The lattice constants were determined by a least-squares fit[10] to these data using the extrapolation function of Nelson and Riley.[11] The values obtained were $a = 7.764 \pm 0.002$, $b = 10.648 \pm 0.002$, $c = 14.780 \pm 0.003$ A, and $\beta = 109.05 \pm 0.02°$, in reasonable agreement with Sternberg's values of $a = 7.76$, $b = 10.66$, $c = 14.76$ A, and $\beta = 109.5°$. The volume of the unit cell is 1154.96 A^3, and the calculated density for two formula units in the unit cell is 1.358 g/cc.

The intensities of 1814 independent reflections (up to $2\theta = 48°$) were measured with a scintillation counter using zirconium-filtered molybdenum Kα radiation. Of these, 1527 reflections had nonzero intensity. A 100-sec scan (with θ, 2θ coupling) covering 3.33° in 2θ was used. The background was obtained from ratemeter charts by averaging the observed background at the beginning and end of the scan for each reflection. A check of the intensities of several reflections selected as standards showed them to remain constant within statistical and instrumental fluctuations during the data-taking period. The Lorentz and polarization corrections were made in the usual manner; no absorption or extinction correction was made. The standard deviation of each intensity measurement was estimated by the formula

$$\sigma^2(I) = C_T + (0.04C_T)^2 + (0.04C_B)^2$$

where C_T and C_B are the total and background counts. The error in the structure factor, $\sigma(F_0)$, was calculated from $\sigma(I)$ by the finite difference method.[12]

Structure Determination

The three-dimensional sharpened Patterson function[13] ($p = 7.25$) showed some partly resolved peaks near the origin which were ascribed to images of the picryl group. Several different combinations of five peaks or positive areas (plus the origin peak) could be chosen as a benzene ring image. A benzene ring of assumed dimensions was fitted to these Patterson peaks by least-squares minimization of the function Σd_i^2, where d_i is the distance between the observed and calculated peak positions. An M_6 minimum function[14] was obtained by superposition on the five calculated peak positions with three-dimensional linear interpolation. The four nitrogens on the picryl ring could be identified on the M_6 map; an M_{10} superposition map was subsequently prepared utilizing these nitrogen positions.

An estimate of the position of the glide plane was made from the M_{10} map; the value obtained was correct within 0.19 A, based on the final structure. No origin was needed in x or z since the space group is polar in both these directions. N(20), O(25), and O(26) were clearly recognizable on the M_{10} map. A careful examination of the multitude of other peaks on the map did not reveal any benzene ring patterns belonging to the other three rings in the structure. We proceeded with the structure analysis by selecting likely looking peaks from the M_{10} map which were geometrically reasonable, and using these along with the 13 definitely identified peaks for many successive trial structures from which Fourier maps were prepared. The two phenyl rings of DPPH were eventually recognized, and finally the benzene of solvation was also found.

A reexamination of the M_{10} map was made by comparison with the atomic locations found in the final structure. It was found that 12 of the 35 possible peaks were missing. The failure of the M_{10} map to exhibit peaks for all atoms is ascribed to inaccuracy of the superposition points selected. While the first five points were correct within 0.15 A, the nitrogen superposition points were found to be incorrect by as much as 0.25 A. This difficulty in turn is due to the well-known problems of resolution and multiplicity of peaks in the Patterson function, and to the incorrectness of the assumption that the o-nitro group nitrogens were coplanar with the other eight atoms.

When all atoms were approximately located, the R factor dropped to 37% for 794 low angle reflections. Several cycles of Fourier refinement reduced the R factor to 24% for 1007 reflections. Least-squares refinement was begun at this point using the full-matrix program of Busing, Martin, and Levy.[15] The scattering factors of Hanson, Herman, Lea, and Skillman[16] were used for C, N, and O and of Stewart, Davidson, and Simpson[17] for H. The hydrogen atoms were placed at calculated positions with an assumed C–H bond length of 1.01 A. The results of the refinement using isotropic temperature factors (139 independent variables) have been previously reported.[9] The R factor for nonzero observations was 8.2% for 1032 reflections.

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Table I. Final Values of the Parameters and Their Estimated Standard Deviations ($\times 10^4$)[a]

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
C(1)	10,039 (9)	2,304 (5)	3062 (4)	163 (13)	61 (6)	36 (3)	−2 (7)	16 (6)	4 (4)
C(2)	8,616 (8)	3,161 (5)	3025 (4)	189 (14)	66 (6)	39 (4)	−7 (8)	18 (6)	−7 (4)
C(3)	6,925 (8)	3,095 (5)	2351 (5)	159 (13)	82 (7)	48 (4)	12 (8)	33 (6)	6 (4)
C(4)	6,524 (9)	2,110 (6)	1700 (4)	150 (13)	91 (7)	39 (3)	5 (8)	13 (6)	3 (4)
C(5)	7,812 (9)	1,203 (5)	1717 (4)	182 (14)	78 (6)	48 (4)	−9 (8)	18 (6)	−6 (4)
C(6)	9,518 (8)	1,336 (5)	2373 (4)	153 (13)	69 (6)	47 (4)	12 (7)	17 (6)	0 (4)
C(7)	12,438 (8)	4,385 (5)	3463 (5)	142 (12)	72 (6)	45 (4)	−1 (7)	13 (5)	0 (4)
C(8)	12,319 (9)	5,548 (6)	3839 (5)	228 (16)	76 (7)	49 (4)	−7 (8)	25 (6)	−7 (5)
C(9)	12,097 (9)	6,602 (6)	3268 (6)	224 (17)	78 (7)	81 (5)	11 (8)	56 (7)	−5 (5)
C(10)	12,017 (10)	6,504 (6)	2331 (6)	255 (17)	86 (7)	83 (6)	30 (9)	65 (8)	25 (5)
C(11)	12,155 (10)	5,340 (6)	1953 (5)	237 (16)	108 (8)	55 (4)	26 (10)	35 (7)	21 (5)
C(12)	12,359 (9)	4,266 (6)	2503 (5)	181 (14)	94 (7)	47 (4)	21 (8)	24 (6)	1 (4)
C(13)	14,113 (9)	3,156 (6)	4913 (4)	145 (13)	97 (7)	36 (3)	14 (8)	5 (6)	−3 (4)
C(14)	14,043 (10)	2,217 (7)	5533 (5)	209 (16)	128 (8)	41 (4)	29 (9)	14 (6)	11 (5)
C(15)	15,456 (11)	2,080 (7)	6386 (5)	276 (18)	127 (9)	56 (4)	42 (11)	2 (8)	12 (5)
C(16)	16,917 (11)	2,888 (9)	6628 (5)	256 (19)	174 (12)	53 (4)	29 (12)	−25 (8)	−5 (6)
C(17)	16,985 (9)	3,832 (8)	6002 (6)	158 (15)	186 (11)	69 (5)	−10 (10)	−9 (7)	−14 (6)
C(18)	15,578 (10)	3,985 (6)	5127 (5)	170 (14)	123 (8)	60 (5)	−7 (9)	9 (7)	−10 (5)
N(19)	11,779 (7)	2,219 (4)	3690 (4)	174 (11)	70 (5)	46 (3)	−2 (6)	2 (5)	1 (3)
N(20)	12,677	3,278 (4)	4029	167 (10)	69 (5)	43 (3)	6 (6)	4 (5)	2 (3)
N(21)	8,804 (9)	4,073 (5)	3792 (5)	209 (13)	84 (6)	63 (4)	−17 (7)	47 (6)	−11 (4)
O(22)	9,801 (7)	3,809 (4)	4606 (4)	262 (12)	141 (6)	54 (3)	−21 (7)	39 (5)	−20 (4)
O(23)	7,879 (8)	5,018 (5)	3589 (4)	306 (14)	87 (5)	104 (4)	28 (7)	53 (6)	−22 (4)
N(24)	4,710 (8)	2,005 (6)	1004 (4)	181 (13)	135 (8)	52 (4)	−10 (9)	25 (6)	−9 (5)
O(25)	3,696 (8)	2,926 (5)	897 (4)	225 (11)	149 (7)	68 (3)	48 (7)	6 (5)	4 (4)
O(26)	4,295 (7)	1,025 (5)	562 (4)	200 (11)	180 (8)	93 (4)	−27 (7)	9 (5)	−59 (5)
N(27)	10,909 (9)	436 (6)	2307 (4)	199 (14)	91 (7)	72 (4)	37 (8)	11 (6)	−9 (4)
O(28)	10,544 (9)	−664 (5)	2308 (5)	413 (17)	72 (5)	166 (6)	33 (8)	62 (7)	−2 (5)
O(29)	12,298 (8)	856 (5)	2214 (4)	217 (11)	144 (6)	92 (4)	44 (8)	37 (6)	−15 (4)
C(30)	9,582 (11)	9,510 (16)	4799 (7)	225 (20)	348 (21)	113 (7)	−47 (19)	53 (10)	77 (12)
C(31)	8,464 (18)	10,513 (9)	4632 (6)	613 (40)	154 (11)	78 (6)	−127 (18)	88 (13)	5 (7)
C(32)	6,624 (15)	10,354 (10)	4154 (6)	429 (28)	194 (13)	81 (6)	143 (16)	92 (10)	47 (7)
C(33)	6,009 (10)	9,188 (11)	3906 (6)	248 (18)	211 (13)	92 (6)	−4 (14)	16 (8)	−13 (8)
C(34)	7,100 (18)	8,228 (9)	4091 (7)	526 (32)	175 (12)	111 (7)	25 (18)	77 (13)	−38 (7)
C(35)	8,890 (17)	8,367 (13)	4557 (7)	448 (34)	297 (20)	112 (8)	228 (21)	118 (15)	45 (10)
H(36)	5,990	3,762	2335	Same as C(3)					
H(37)	7,514	465	1263	Same as C(5)					
H(38)	12,395	5,629	4531	Same as C(8)					
H(39)	11,992	7,458	3540	Same as C(9)					
H(40)	11,857	7,283	1922	Same as C(10)					
H(41)	12,107	5,273	1263	Same as C(11)					
H(42)	12,447	3,419	2213	Same as C(12)					
H(43)	12,961	1,631	5363	Same as C(14)					
H(44)	15,420	1,379	6840	Same as C(15)					
H(45)	17,930	2,788	7259	Same as C(16)					
H(46)	18,071	4,414	6185	Same as C(17)					
H(47)	15,619	4,674	4665	Same as C(18)					
H(48)	10,942	9,614	5105	Same as C(30)					
H(49)	8,995	11,367	4860	Same as C(31)					
H(50)	5,740	11,081	3989	Same as C(32)					
H(51)	4,672	9,026	3565	Same as C(33)					
H(52)	6,556	7,374	3874	Same as C(34)					
H(53)	9,717	7,610	4724	Same as C(35)					

[a] The form of the temperature factor is $\exp(-\beta_{11}h^2 - \beta_{22}k^2 - \beta_{33}l^2 - 2\beta_{12}hk - 2\beta_{13}hl - 2\beta_{23}kl)$.

For the anisotropic refinement it was necessary because of computer limitations to refine on alternate cycles the scale factor and the DPPH molecule (260 independent variables) and the scale factor and the benzene molecule (55 independent variables). The temperature factors of the hydrogens were set equal to the atom to which they were bonded.

The x and z of atom N(20) were not varied to define the polar origin. Convergence was observed to be satisfactory in the y parameters, thermal factors, and scale factor but slow in the polar x and z parameters. Double shifts were subsequently used for the x and z parameters. The refinement was continued until the magnitudes of all shifts were less than 0.2σ; at this point only 7 of the 314 shifts exceeded 0.1σ in magnitude.

Inversion of the 260×260 matrix of the normal equations was carried out in single precision (24 binary bits carried) using the method of Busing and Levy.[18] A check was made for rounding error by multiplying the matrix by its inverse. The maximum difference between the result and a unit matrix was 1.8×10^{-4}. Since errors in the matrix inversion affect primarily only the shifts in the parameters rather than the values of the parameters themselves, this result is regarded as satisfactory.

A three-dimensional difference Fourier map was prepared from the final model; the values on this map varied in an apparent random fashion from −0.29 to +0.27 e/A^3. No peak was found in the vicinity of

(18) W. R. Busing and H. A. Levy, *Comm. ACM*, **5**, 445 (1962).

N(19) where a hydrogen atom would be located in the corresponding hydrazine molecule.

A list of the observed structure factors and their estimated errors and the final calculated structure factors is available.[19] The final unweighted R factor for nonzero data was 0.071 for 1527 reflections. The weighted R factor for all 1814 reflections was 0.045. The final values of the parameters and their estimated standard deviations are given in Table I.

Molecular Structure

The shape of the DPPH molecule in the DPPH-C_6H_6 crystal is shown in Figure 1. The bond distances, angles, and their estimated standard deviations are shown in Table II. Covariances between parameters were included in the error treatment,[20] except those between parameters of different molecules.

Table II. Bond Distances (A) and Angles (deg) and Their Estimated Standard Deviations

Atoms	Distance	Atoms	Distance
C(1)C(2)	1.420 (7)	N(19)N(20)	1.334 (6)
C(2)C(3)	1.366 (7)	N(20)C(7)	1.422 (7)
C(3)C(4)	1.389 (8)	N(20)C(13)	1.419 (6)
C(4)C(5)	1.384 (8)	C(2)N(21)	1.463 (7)
C(5)C(6)	1.370 (7)	N(21)O(22)	1.232 (6)
C(6)C(1)	1.412 (7)	N(21)O(23)	1.216 (6)
C(7)C(8)	1.373 (7)	C(4)N(24)	1.452 (7)
C(8)C(9)	1.380 (8)	N(24)O(25)	1.236 (7)
C(9)C(10)	1.370 (9)	N(24)O(26)	1.217 (7)
C(10)C(11)	1.378 (9)	C(6)N(27)	1.471 (7)
C(11)C(12)	1.382 (8)	N(27)O(28)	1.205 (6)
C(12)C(7)	1.405 (7)	N(27)O(29)	1.217 (7)
C(13)C(14)	1.369 (8)	C(30)C(31)	1.348 (13)
C(14)C(15)	1.383 (8)	C(31)C(32)	1.382 (11)
C(15)C(16)	1.375 (10)	C(32)C(33)	1.338 (11)
C(16)C(17)	1.379 (10)	C(33)C(34)	1.298 (11)
C(17)C(18)	1.403 (8)	C(34)C(35)	1.343 (13)
C(18)C(13)	1.393 (8)	C(35)C(30)	1.331 (13)
C(1)N(19)	1.370 (6)		
Atoms	**Angle**	**Atoms**	**Angle**
C(1)C(2)C(3)	123.1 (5)	N(20)C(7)C(8)	121.5 (5)
C(2)C(3)C(4)	119.2 (5)	N(20)C(13)C(14)	119.5 (5)
C(3)C(4)C(5)	121.2 (5)	N(20)C(13)C(18)	119.3 (5)
C(4)C(5)C(6)	117.8 (5)	C(1)C(2)N(21)	121.1 (5)
C(5)C(6)C(1)	124.7 (5)	C(3)C(2)N(21)	115.3 (5)
C(6)C(1)C(2)	113.9 (4)	C(2)N(21)O(22)	118.5 (5)
C(7)C(8)C(9)	119.9 (6)	C(2)N(21)O(23)	117.2 (6)
C(8)C(9)C(10)	120.7 (6)	O(22)N(21)O(23)	124.2 (6)
C(9)C(10)C(11)	119.7 (6)	C(3)C(4)N(24)	119.7 (6)
C(10)C(11)C(12)	120.9 (6)	C(5)C(4)N(24)	119.1 (6)
C(11)C(12)C(7)	118.6 (6)	C(4)N(24)O(25)	117.4 (6)
C(12)C(7)C(8)	120.2 (6)	C(4)N(24)O(26)	118.1 (6)
C(13)C(14)C(15)	119.7 (6)	O(25)N(24)O(26)	124.5 (6)
C(14)C(15)C(16)	120.9 (7)	C(5)C(6)N(27)	116.6 (5)
C(15)C(16)C(17)	119.4 (6)	C(1)C(6)N(27)	118.7 (5)
C(16)C(17)C(18)	120.9 (6)	C(6)N(27)O(28)	117.1 (6)
C(17)C(18)C(13)	117.9 (6)	C(6)N(27)O(29)	117.7 (6)
C(18)C(13)C(14)	121.2 (5)	O(28)N(27)O(29)	125.1 (6)
C(2)C(1)N(19)	130.6 (5)	C(30)C(31)C(32)	119.5 (9)
C(6)C(1)N(19)	115.3 (5)	C(31)C(32)C(33)	118.1 (8)
C(1)N(19)N(20)	118.5 (4)	C(32)C(33)C(34)	121.5 (8)
N(19)N(20)C(7)	121.8 (4)	C(33)C(34)C(35)	121.1 (10)
N(19)N(20)C(13)	115.1 (4)	C(34)C(35)C(30)	119.9 (10)
C(7)N(20)C(13)	122.0 (4)	C(35)C(30)C(31)	119.7 (9)
N(20)C(7)C(12)	118.3 (5)		

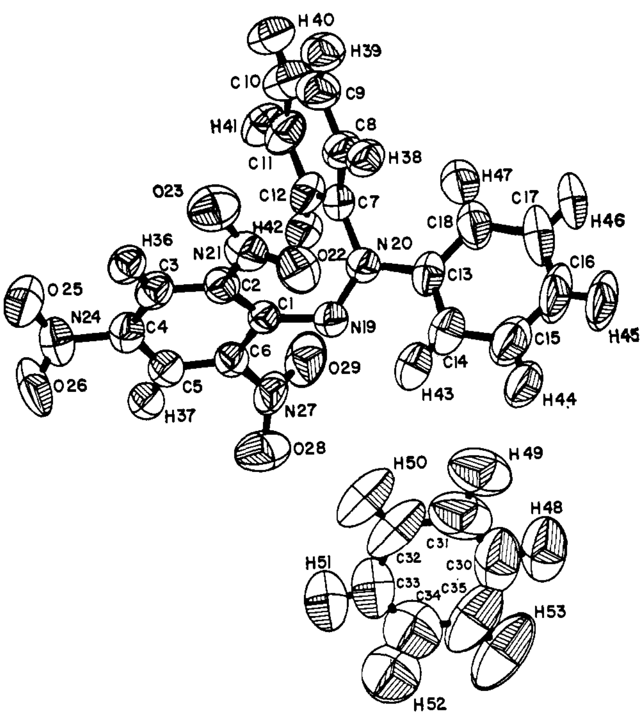

Figure 1. The molecular structure. The thermal ellipsoids enclose a probability density[22] of 0.62. The DPPH and benzene molecules are on the same scale and are in the same relative angular orientation as in the cell, but the benzene molecule has been translated to eliminate overlap. See Figure 2 for the packing positions of the benzene molecules.

The configuration around N(20) is approximately trigonal, with angles N(19)N(20)C(7) = 121.8°, N(19)N(20)C(13) = 115.1°, and C(7)N(20)C(13) = 122.0°. There is a small but experimentally significant deviation from planarity, with N(20) being 0.080 A in front of the plane formed by C(7), C(13), and N(19) (Figure 1). The equation of the best least-squares plane through the four atoms is $0.8500X - 0.2896Y - 0.4400Z = 3.2872$ A, where the Cartesian reference axes X, Y, and Z are taken parallel to a, b, and c^*. The atomic deviations from this least-squares plane are -0.021, -0.019, -0.021, and 0.060 A for C(7), C(13), N(19), and N(20), respectively.

The C(1)N(19)N(20) bond angle is 118.5°. The equation of the plane passing through these atoms is $0.6433X + 0.0165Y - 0.7654Z = 0.8308$ A. The angle between this plane and the C(7)C(13)N(19)N(20) plane is 28.5°. The twist angles along the N(19)–N(20) bond are 34.3 for C(1)N(19)N(20)C(7) and 156.9° for C(1)N(19)N(20)C(13). (The twist angle ABCD is defined as the angle between the vectors (AB) × (BC) and (BC) × (CD).)

The equations for the best least-squares planes[21] for the four benzene rings in the structure are given in Table III. The phenyl rings C(7)–C(12) and C(13)–C(18) are accurately planar; the minimum C–C distance in the two rings is 1.369 A and the maximum is 1.405 A. The minimum and maximum C–C–C angles are 117.9 and 121.2°. These figures do not show any significant

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Table III. Deviation from the Least-Squares Planes (A)

Plane C(1)–C(6)		Plane C(7)–C(12)		Plane C(13)–C(18)		Plane C(30)–C(35)	
Atom	Dev	Atom	Dev	Atom	Dev	Atom	Dev
C(1)	−0.011	C(7)	−0.003	C(13)	−0.001	C(30)	−0.020
C(2)	0.023	C(8)	0.006	C(14)	−0.004	C(31)	0.014
C(3)	−0.013	C(9)	−0.003	C(15)	−0.006	C(32)	−0.003
C(4)	−0.009	C(10)	−0.002	C(16)	0.004	C(33)	−0.002
C(5)	0.020	C(11)	0.004	C(17)	−0.000	C(34)	−0.004
C(6)	−0.010	C(12)	−0.002	C(18)	−0.002	C(35)	0.016

Plane C(1)–C(6) $0.5304X + 0.5588Y - 0.6375Z = 1.9840$
Plane C(7)–C(12) $0.9559X + 0.1008Y + 0.2757Z = 9.4421$
Plane C(13)–C(18) $0.6546X - 0.6124Y - 0.4432Z = 0.5227$
Plane C(30)–C(35) $-0.4598X - 0.1150Y + 0.8805Z = 2.4024$

deviation from a regular hexagon with sides of length 1.383 A.

N(20) is coplanar with both phenyl rings C(7)–C(12) and C(13)–C(18) The plane of ring C(7)–C(12) is inclined at 48.5° to the C(7)C(13)N(19)N(20) plane. The twist angle N(19)N(20)C(7)C(12) (42.7°) is smaller than the twist angle C(13)N(20)C(7)C(8) (53.5°) because of the slight nonplanarity around N(20). The plane of ring C(13)–C(18) is inclined at 21.7° to the C(7)-C(13)N(19)N(20) plane. The twist angle N(19)N(20)-C(13)C(14) is 26.5° and the twist angle C(7)N(20)-C(13)C(18) is 16.0°.

In the picryl ring the C–C distances are not as uniform, with a minimum of 1.366, a maximum of 1.420, and mean distance of 1.390 A. The plane of the picryl ring is inclined at 33.0° to the C(1)N(19)N(20) plane. The twist angles C(2)C(1)N(19)N(20) and C(6)C(1)-N(19)N(20) are 36.8 and 148.2°, respectively. N(19) is in front of the picryl ring mean plane by 0.044 A (Figure 1). This deviation is such that the picryl ring is bent forward slightly away from the C(7)–C(12) phenyl ring, as if the C(1)N(19)N(20) angle were slightly strained toward a larger value. Angle N(19)C(1)C(2) has also increased to 130.6° and angle N(19)C(1)C(6) has decreased to 115.3°. The deviations of C(2) (0.023 A) and C(6) (−0.010 A) from the picryl ring least-squares plane are in the same direction as the nitrogens in the *o*-nitro groups.

N(24) is accurately coplanar with the picryl ring; the nitrogens in the *o*-nitro groups are not coplanar, the deviations being 0.283 for N(21) and −0.122A for N(27). The deviation of N(21) relieves the distances N(21)–C(7) = 3.03 and N(21)–C(8) = 3.13 A; the distances N(21)–N(19) and N(21)–N(20) are 3.08 and 3.03 A, respectively. N(27) deviates in the correct direction to relieve the O(29)–N(19) distance of 2.76 A. The unshared electron pair on N(19) also could push O(29) away, giving a negative deviation to N(27) from the picryl ring plane. These arguments presuppose a tendency of the nitro groups to become coplanar with the benzene ring. The angles C(1)C(2)N(21) and C(1)-C(6)N(27) are 121.1 and 118.7°, indicating that the *o*-nitro groups resist being pushed back toward the *para* end of the picryl ring.

The N–O and C–N distances of the nitro groups are all quite similar with means of 1.221 and 1.462 A, respectively. The O–N–O angles are also quite similar with a mean of 124.6°. The angles between the planes of the nitro groups and the picryl ring plane are 24.8, 13.4, and 54.5° for N(21)O(22)O(23), N(24)O(25)O(26), and N(27)O(28)O(29), respectively. Presumably the smaller twist of the *p*-nitro group is to allow better intermolecular packing. Twist angle C(1)C(2)N(21)O(22) is 28.1° and twist angle C(1)C(6)N(27)O(29) is 53.2°. These twists are in a direction to relieve the distances O(22)–N(20) = 2.70, O(22)–N(19) = 2.90, O(22)–C(7) = 3.11, O(22)–C(8) = 3.16, and O(29)–N(19) = 2.76 A. Angles C(2)N(21)O(22) and C(6)N(27)O(29) are normal at 118.5 and 117.7°, respectively.

Packing Structure and Thermal Motion

The shortest C···C intermolecular approach is C(31)–C(1) = 3.52 A, the shortest C···H approach is C(31)–H(37) = 2.93 A, and the shortest H···H approach is H(48)–H(43) = 2.61 A. There are no C···N approaches less than 3.20, and the shortest C···O intermolecular distance is O(26)–C(33) = 3.15 A. There is an O···H distance O(26)–H(48) = 2.56 A, but no N···H, N···O, N···N, or O···O distances less than 2.80 A. Table IV gives a complete listing of the short intermolecular distances classified by symmetry type. Distances involving hydrogen are based on calculated hydrogen positions. Figure 2 shows how the molecules pack together in the crystal.

Table IV. Short Intermolecular Distances (A) Classified by Symmetry Type[a]

1. No symmetry
   O(23)H(52), 2.80
2. Translation *a*
   C(12)H(36), 2.96; H(39)H(51), 2.66; H(42)O(25), 2.50; H(42)H(36), 2.72; H(47)O(23), 2.75.
3. Translation *b*
   C(31)C(1), 3.52; H(39)O(28), 2.69; H(40)O(28), 2.55; H(48)H(43), 2.61; H(49)C(1), 3.18; H(49)O(22), 2.73
4. Translations a, $-b$
   N(19)H(50), 3.20
5. Glide plane at $y = 0$, translations a, $c/2$
   C(15)H(37), 3.18
6. Glide plane at $y = b/2$, translation $c/2$
   C(14)H(40), 3.11; O(22)H(41), 2.70; C(30)H(37), 3.09; C(31)H(37), 2.93; C(32)H(37), 3.09
7. Glide plane at $y = b/2$, translation $-c/2$
   C(5)C(35), 3.58; O(26)C(33), 3.15
8. Glide plane at $y = b/2$, translations $-a$, $-c/2$
   C(9)H(45), 3.16; C(10)H(46), 3.13; C(11)H(46), 3.01; O(25)H(38), 2.48; O(26)H(48), 2.56; C(33)H(44), 3.00; C(34)H(44), 3.18; C(34)H(45), 3.17
9. Glide plane at $y = b/2$, translations $-a$, $c/2$
   H(50)C(13), 3.08

[a] The specified symmetry operation is applied to the second atom of the pair. There is an equivalent distance with the atoms interchanged, using the same symmetry operation with a negative translation part. All distances are included up to a carbon radius of 1.80 A and a radius of 1.40 A for all other types of atoms.

The intermolecular distances indicate that there is no strong "complex" formed between DPPH and benzene, or between DPPH molecules, in this structure. The benzene molecules of solvation fit into spaces between the irregularly shaped DPPH molecules. The volume of the cell (1154.96 A^3) is slightly greater than the sum of the corresponding packing volumes of solvent-free orthorhombic DPPH and benzene at $-3°$ (1134.87 A^3), again indicating no strong interaction with the solvate. In fact, the slight increase in packing volume is consistent with the observed large thermal amplitude for benzene in this structure.

Figure 1 shows the orientation of the thermal ellipsoids as plotted by the computer program of Johnson.[22] The observed anisotropic thermal amplitudes for the DPPH molecule were in the normally expected range, with a minimum root-mean-square amplitude of 0.17 and a maximum of 0.35 A, if the nitro oxygens are excluded. The estimated standard deviation of the thermal amplitudes is 0.01 A. The terminal nitro oxygens were expected to show larger thermal amplitudes, the largest observed being 0.42 A for O(28). The thermal amplitudes show a definite pattern of increase as one moves away from the center of the DPPH molecule.

We have fitted the anisotropic thermal amplitudes of the DPPH molecule to a rigid body model by the method of Cruickshank;[23] the numerical results obtained for the translation and libration tensors are available.[19] We would expect the rigid body model to be poor for DPPH because of molecular flexibility. Molecular models indicate, however, considerable stiffening of the molecule because of intramolecular repulsions. The values obtained for translation and libration of the DPPH molecule are in the normally expected range.

The observed anisotropic thermal amplitudes of the carbons in the benzene of solvation reach a maximum root-mean-square amplitude of 0.49 A for atom C(35). Associated with this large thermal motion is a foreshortening of the mean C–C bond distance to 1.34 A. This result would be expected if the benzene had a large amplitude of oscillation about its sixfold axis such as has been observed and analyzed for crystalline benzene[24] itself. Examination of the orientation of the thermal ellipsoids revealed that the tangential component was larger than the radial or out-of-plane components (Figure 1).

When rigid body analysis of the benzene thermal motion was attempted, physically meaningless results were obtained corresponding to a very large translation along with negative mean-square librational amplitudes for two axes. It was found that, if the translation tensor was constrained to be isotropic, apparently good results could be obtained for the libration tensor. The major axis of libration obtained in this way is directed approximately normal to the ring plane (the difference in directions is 19.5°) and is of amplitude 14°. This librational amplitude would be expected to foreshorten[25] the C–C distances by about 0.04 A as is observed.

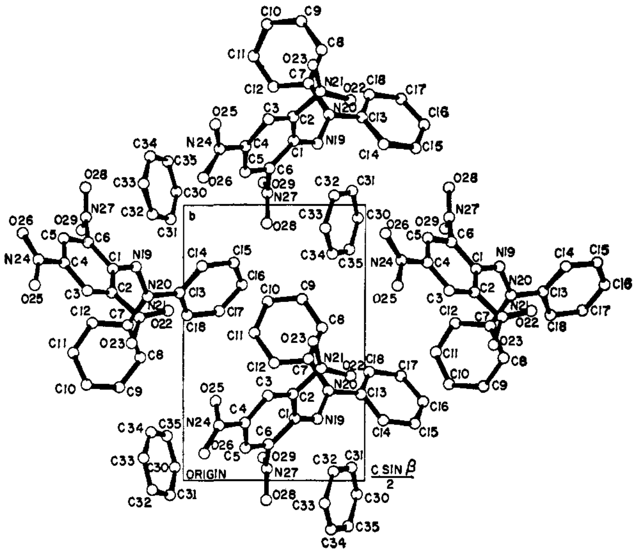

Figure 2. The packing structure.

The observed librational amplitude of the benzene about its sixfold axis is larger than in crystalline benzene[26] itself slightly below its melting point (7.9° libration at $-3°$). To test the possibility that the benzene might be essentially freely rotating or statistically disposed, we attempted to refine a model in which half-carbon atoms were placed at the corners of a dodecagon. Poor results were obtained with the R index increasing by 2%. Also, there have appeared a number of reports[27] that less than a stoichiometric amount of benzene is present in the DPPH–C_6H_6 crystal. To test this possibility we assigned a population parameter to the benzene and attempted to refine this parameter. The least-squares treatment caused the population parameter to *increase* to 1.015, thus giving no support to the thesis that less than a stoichiometric amount of benzene is present. In addition, the final difference Fourier map showed no significant peaks or holes in the vicinity of the benzene molecule.

We concluded that it is likely that a stoichiometric amount of benzene is present and that the molecules are ordered, except possibly for occasional 60° flips, with a large librational amplitude about the sixfold axis. Such occasional 60° flips of benzene molecules have been detected in crystalline benzene itself by analysis of the pmr line width and spin-lattice relaxation time.[28]

Discussion

The N–N bond length of 1.334 A is considerably less than observed in hydrazine[29a] itself (1.45 A) but is longer than the expected value[29b] for a double bond (1.23 A). The observed bond length is thus consistent

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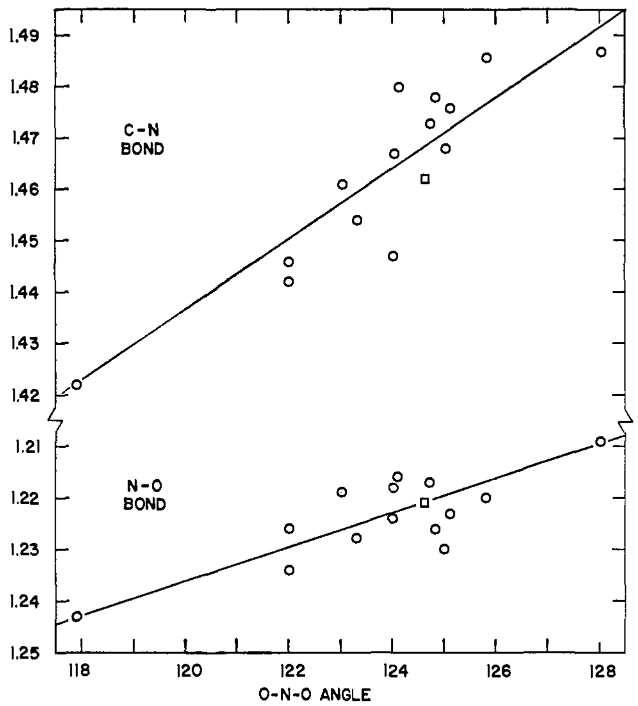

Figure 3. Nitro group C–N and N–O distances *vs.* the O–N–O angle. The values obtained in the present study are indicated by the square symbols.

with the expected value for a three-electron bond between the nitrogen atoms.

The approximately planar configuration around N(20) was widely predicted on grounds of conjugative stabilization of the molecule and on the basis of epr measurements. The crystal structures of triphenylamine[30] or 1,1-diphenylhydrazine have not been determined. Crystalline triphenylphosphorus[31] has a pyramidal molecular configuration with C–P–C angles of 103°. An electron diffraction study of triphenylamine,[32] however, concluded that the bonds around the nitrogen were nearly planar, with C–N–C angles of 116 ± 2°.

The two phenyl–nitrogen distances (1.422 and 1.419 A) are nearly identical and thus do not show any correlation with the phenyl twist angles. These distances may be compared with the C–N distances in triphenylamine[32] (1.42 A), *p*-chloroaniline[33] (1.40 A), and 2,5-dichloroaniline[34] (1.40 A).

The addition of nitro groups to aromatic amines typically shortens the amine C–N distance; in *p*-nitroaniline[35] this distance is 1.353 A. When *o*-nitro groups are present the amine C–N distance further decreases to 1.312 A in 2,3,4,6-tetranitroaniline[36] and 1.316 A in 1,3,5-triamino-2,4,6-trinitrobenzene.[37] Thus, the shortening of the picryl–nitrogen bond in DPPH to 1.370 A is actually less than is observed in the above-mentioned nitroamines. There also is a significant decrease in the C(2)C(1)C(6) bond angle to 113.9° in DPPH, along with the longer C(2)–C(1) and C(6)–C(1) distances of 1.420 and 1.412 A. A similar effect is observed in 2,3,4,6-tetranitroaniline, where the corresponding angle and distances are 114° and 1.434 and 1.428 A.

A literature search failed to turn up any reference correctly predicting a bent rather than a linear bond at N(19). Since the bent bond introduces additional intramolecular steric strain, we concluded that a strong directed valence must be present. With the bent geometry the unshared electron pair is allowed to occupy an sp^2 orbital rather than a higher energy pure p orbital. Even though considerable twisting of the *o*-nitro groups occurs, a rotation of 28.5° about the N(19)–N(20) bond is still required to relieve intramolecular steric strain. The resulting nonplanarity of C(1) was not predicted by analyses of epr measurements.[3]

The observed twists of the rings apparently reflect a compromise between nonbonded repulsions favoring nonplanarity and conjugation favoring planarity. Only one phenyl ring is at a favorable twist angle (22°) for conjugative stabilization. A recent molecular orbital treatment[38] for DPPH included estimates of the ring twist angles; a linear bond at N(19) was assumed, however.

Epr measurements indicate that the unpaired electron is primarily localized about equally on N(19) and N(20). The exceptional unreactivity of DPPH may be explained in that the reactive sites of the molecule are well shielded by surrounding parts of the molecule. N(19) is closely surrounded by C(13) (2.32), C(6) (2.35), C(7) (2.41), H(43) (2.42), C(2) (2.54), N(27) (2.71), H(42) (2.72), O(29) (2.76), O(22) (2.90), C(12) (2.92), and N(21) (3.08 A). N(20) is closely surrounded by C(1) (2.32), C(14) (2.41), C(12) (2.43), C(18) (2.43), C(8) (2.44), H(43) (2.59), H(47) (2.63), H(42) (2.64), H(38) (2.64), O(22) (2.70), C(2) (3.02), and N(21) (3.03 A).

Conjugation involving the nitro groups of the picryl ring is probably not very important in stabilizing the molecule. Removal of the *p*-nitro group, which is at the most favorable angle for conjugation, has little effect and actually makes the radical less reactive toward diphenylamine.[39] On the other hand, removal of one of the *o*-nitro groups results in a large increase in reactivity. Thus it appears that the primary role of the *o*-nitro groups is steric hindrance.[40a]

If this is correct, other groups having similar steric requirements could be substituted. The radical having methyl groups instead of nitro groups has been synthesized but was found to dimerize rapidly to the corresponding tetrazane.[41] A somewhat larger group, such as –CF$_3$ or –C(CH$_3$)$_3$, would better test the hypothesis that the main stabilization provided by the *o*-nitro groups is steric hindrance.

An example of a nonconjugated stable free radical is provided by di-*t*-butyl nitroxide, which has a N–O

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Table V. Geometry of the Aromatic Nitro Group[a]

Crystal	Ref	O–N–O angle	C–N bond	N–O bond	Twist angle
1,3,5-Triamino-2,4,6-trinitrobenzene	37	117.9 (4)	1.422 (7) 1.426[b]	1.243 (6) 1.266[b]	3.8, 3.3, 1.6
α-p-Nitrophenol	*c*	122.0 (4)	1.442 (6)	1.234 (6)	1.5
β-p-Nitrophenol	*d*	122.0 (4)	1.446 (3) 1.450[b]	1.226 (5) 1.242[b]	7.1
2,3,4,6-Tetranitroaniline (no. 6)	36	123.0 (4)	1.461 (7)	1.219 (7)	3
p-Nitroaniline	35	123.3 (4)	1.454 (7)	1.228 (7)	1.9
2,3,4,6-Tetranitroaniline (no. 4)	36	124.0 (4)	1.447 (7)	1.224 (7)	19
2,3,4,6-Tetranitroaniline (no. 2)	36	124.0 (4)	1.467 (7)	1.218 (7)	45
p-Nitrobenzoic acid	*e*	124.1 (4)	1.480 (7)	1.216 (6)	13.7
2,2-Diphenyl-1-picrylhydrazyl	This work	124.6 (6)	1.462 (7)	1.221 (7)	13.4, 24.8, 54.5
1,3,5-Trinitrobenzene–azulene	*f*	124.7 (2)	1.473 (3) 1.480[b]	1.217 (3) 1.243[b]	"Not planar"
o-Nitroperoxybenzoic acid	*g*	124.8 (5)	1.478 (7)	1.226 (7)	28
o-Nitrobenzaldehyde	*h*	125.0 (6)	1.468 (8)	1.230 (6)	27.5
1,3,5-Trinitrobenzene–acepleiadylene	*i*	125.1	1.476 (3) 1.477[b]	1.223 (3) 1.233[b]	"Not planar"
m-Dinitrobenzene	*j*	125.8 (4)	1.486 (8) 1.493[b]	1.220 (9) 1.248[b]	13
2,3,4,6-Tetranitroaniline (no. 3)	36	128.0 (4)	1.487 (7)	1.209 (7)	64

[a] Angles given in degrees and bonds in angstroms. [b] Thermally corrected distance. [c] P. Coppens and G. M. J. Schmidt, *Acta Cryst.*, **18**, 62 (1965). [d] P. Coppens and G. M. J. Schmidt, *ibid.*, **18**, 654 (1965). [e] T. D. Sakore and L. M. Pant, *ibid.*, **21**, 715 (1966). [f] A. W. Hanson, *ibid.*, **19**, 19 (1965). [g] M. Sax, P. Beurskens, and S. Chu, *ibid.*, **8**, 252 (1965). [h] P. Coppens and G. M. J. Schmidt, *ibid.*, **17**, 222 (1964). [i] A. W. Hanson, *ibid.*, **21**, 97 (1966). [j] J. Trotter and C. S. Williston, *ibid.*, **21**, 585 (1966).

bond length corresponding to a three-electron bond. This radical is also made unreactive by steric hindrance.[40b]

As has been observed for other aromatic nitro compounds, there is no significant correlation of the C–NO_2 distance with the nitro twist angle.[42] It has been pointed out by Trueblood, Goldish, and Donohue[35] and by Coppens[43] that there is a correlation between the O–N–O angle and the C–N distance in aromatic nitro compounds. This correlation was thought to be caused by nonbonded interaction[44] between C and O. Table V summarizes the available data where the estimated standard deviations in the bond lengths are 0.01 A or less. Figure 3 shows that there also is a correlation between the O–N–O angle and the N–O distance.

There are three methods currently being used to thermally correct bond distances in crystals: the "independent" and "riding" atomic models of Busing and Levy,[45] and the rigid molecule model of Cruickshank.[25] None of these models is expected to give a completely accurate correction for the complicated situation of the C–N and N–O bond distances in nitro groups. We have chosen, therefore, to compare thermally uncorrected distances in Table V and Figure 3. The correlation of the C–N and N–O distances with the O–N–O angle will remain if the thermal correction is approximately the same for all distances of a given type. Because of the observed torsional oscillation about the C–N bond, the correction would be larger for the N–O distances.

The changes in the C–N distance are much larger than the thermal correction for these distances. If the shortening of the N–O bond were a thermal effect, the correction would have to be ~0.03 A larger for 2,3,4,6-tetranitroaniline nitro group no. 3 than for 1,3,5-triamino-2,4,6-trinitrobenzene. Examination of the thermal parameters of these compounds does not indicate a larger thermal motion for the nitro group in the former compound. Also, the thermal correction for the O–N–O bond angle is expected to be negligible.

The changes in both the C–N and N–O distances may be explained by analysis of the sp^2 hybridization at the nitrogen atom. We expect the bond length to decrease with increasing s character of the bond.[46] If ϕ is the (symmetrical) O–N–O angle, the amount of s character in the orbitals pointing toward the oxygens is given by $-\cos\phi/(1 - \cos\phi)$. In going from $\phi = 118$ to 128° the s character increases from 32 to 38%. On the other hand, the s character of the bond to carbon is given by $\cos^2(\phi/2)/(\cos^2(\phi/2) - \cos\phi)$, and it decreases from 36 to 24% consistent with the observed increase in the C–N bond length. The hybridization argument also correctly predicts the observed 2 : 1 ratio of the bond length changes.

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