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Crystal Structure Determination by Neutron Diffraction of 2,2-Diphenyl-1-picrylhydrazyl (DPPH) Benzene Solvate (1/1)

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Abstract. The crystal structure of 2,2-diphenyl-1-picrylhydrazyl (DPPH), syncrystallized with one benzene molecule per DPPH molecule (DPPH–C_6H_6), already determined at room temperature with X-rays [Williams (1967). *J. Am. Chem. Soc.* **89**, 4280–4287], was remeasured at low temperature (10 K) by neutron diffraction. Crystal data: $C_{18}H_{12}N_5O_6.C_6H_6$, $M_r = 472{\cdot}45$, monoclinic, Pc, $a = 7{\cdot}583\,(10)$, $b = 10{\cdot}593\,(15)$, $c = 14{\cdot}526\,(20)$ Å, $\beta = 108{\cdot}47\,(6)°$, $V = 1104{\cdot}57\,(2{\cdot}65)$ Å^3, $Z = 2$, $D_x = 1{\cdot}420$ g cm^{-3}, $\lambda = 1{\cdot}176$ Å, $R = 0{\cdot}032$ for 1264 unique observed reflections. The positions of the H atoms have been determined as well as the values of the temperature factors at 10 K. The shape of the molecule does not change significantly on cooling from room to low temperature.

Introduction. The stable aromatic free radical 2,2-diphenyl-1-picrylhydrazyl (DPPH) was one of the first paramagnetic species investigated by electron spin resonance. Its chemical stability and the narrowness of its resonance have led to the widespread use of its powder form as a standard in measuring unpaired spin concentrations and effective gyromagnetic ratios (Buchachenko, 1965). In addition, the hyperfine structure of the DPPH radical has been one of the most thoroughly investigated using magnetic resonance techniques (Maruani, 1980). Consequently DPPH appears as a very good candidate for a complete spin-density determination using polarized neutron diffraction, in order to compare the local values of the spin density given by the resonance techniques with the spin-density distribution, measured at each point of the molecule, by neutron diffraction (Boucherle, Gillon, Maruani & Schweizer, 1982).

DPPH is known in several forms (Weil & Anderson, 1965). Some of them are solvent free: DPPH-I (m.p. 379 K) is orthorhombic (Williams, 1965),

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DPPH-II (m.p. 410 K) is amorphous and DPPH-III (m.p. 401–402 K) is triclinic (Williams, 1965). Some others contain molecules of solvation: DPPH-III*a* (m.p. 400–401 K) is also triclinic and contains one acetone molecule to four DPPH molecules (Kiers, de Boer, Olthof & Spek, 1976) and DPPH–C_6H_6 (m.p. 408 K) is monoclinic (Williams, 1966) with one benzene molecule to one DPPH molecule. Only the crystal structures of the last two forms have been investigated. For the spin-density neutron diffraction experiment, the DPPH–C_6H_6 form appeared to be best suited, because it is possible to align more spin in this form than in other DPPH forms, at low temperature, in a magnetic field. The complete structure of this form has been determined by Williams (1967) from X-ray diffraction, at room temperature. This structure belongs to the space group *Pc*, with two DPPH molecules and two benzene molecules per unit cell. The DPPH molecule is shown to consist of a non-planar hydrazyl backbone, linked to one picryl and two phenyl rings, the plane of each of these rings being twisted out of the trigonal coordination plane of the corresponding N atom (see Fig. 1).

The determination of the spin-density distribution from polarized neutron data requires a precise knowledge of the crystal structure at very low temperature, including the positions of H nuclei and the values of the vibration parameters. This led us to undertake first a non-polarized neutron diffraction experiment on a low-temperature DPPH–C_6H_6 single crystal, in order to refine its structure. In this paper we present the results of this investigation.

Experimental. DPPH–C_6H_6 single crystals were prepared by slow cooling of a benzene–hexane solution saturated with commercial DPPH. To prevent any possible benzene evaporation the crystals were kept in the dark in a refrigerator.

A needle-shape crystal was selected with dimensions 3·3 × 0·5 × 0·5 mm, with its long axis along **a**. The crystal was mounted on the four-circle neutron diffractometer D15 of the ILL. This diffractometer is installed on an inclined beam of the reactor, where the monochromator produces a monochromatic beam ($\lambda = 1{\cdot}176$ Å) in the horizontal plane. The sample was introduced into a double-stage refrigerator and cooled to 10 K. The lattice constants at this temperature, obtained from 12 reflections in the range $8 < \theta < 20{\cdot}6°$, are given in Table 1 together with those determined at room temperature by Williams (1967).

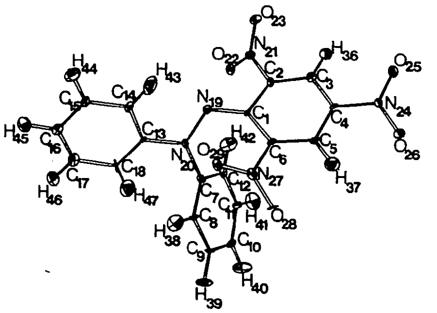

Fig. 1. DPPH molecule with thermal ellipsoids at the 50% probability level.

Table 1. *Lattice constants of DPPH–*C_6H_6

$T = 300$ K (Williams, 1967)	$T = 10$ K (this work)
$a = 7{\cdot}764\ (2)$ Å	$a = 7{\cdot}583\ (10)$ Å
$b = 10{\cdot}648\ (2)$ Å	$b = 10{\cdot}593\ (15)$ Å
$c = 14{\cdot}780\ (3)$ Å	$c = 14{\cdot}526\ (20)$ Å
$\beta = 109{\cdot}05\ (2)°$	$\beta = 108{\cdot}47\ (6)°$
$V = 1154{\cdot}96\ (46)$ Å^3	$V = 1104{\cdot}57\ (2{\cdot}65)$ Å^3

Table 2. *Atomic coordinates*

$$B_{\rm eq} = \tfrac{8}{3}\pi^2 \textstyle\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	*y*	*z*	$B_{\rm eq}$(Å^2)	*PP*
C(1)	29 (6)	2292 (3)	3067 (3)	0·17	1·0
C(2)	8557 (6)	3166 (3)	3021 (3)	0·31	1·0
C(3)	6813 (7)	3096 (3)	2327 (3)	0·36	1·0
C(4)	6439 (6)	2080 (4)	1678 (3)	0·33	1·0
C(5)	7763 (6)	1173 (4)	1688 (3)	0·35	1·0
C(6)	9509 (6)	1337 (4)	2361 (3)	0·32	1·0
C(7)	2469 (6)	4396 (3)	3478 (3)	0·31	1·0
C(8)	2354 (7)	5562 (3)	3879 (3)	0·33	1·0
C(9)	2130 (7)	6643 (3)	3290 (3)	0·44	1·0
C(10)	2075 (6)	6539 (4)	2329 (3)	0·40	1·0
C(11)	2229 (7)	5343 (4)	1937 (3)	0·49	1·0
C(12)	2407 (6)	4257 (4)	2506 (3)	0·37	1·0
C(13)	4142 (6)	3158 (4)	4954 (3)	0·26	1·0
C(14)	4035 (7)	2147 (4)	5576 (3)	0·48	1·0
C(15)	5506 (6)	2008 (4)	6448 (3)	0·44	1·0
C(16)	7015 (6)	2845 (4)	6706 (3)	0·43	1·0
C(17)	7088 (6)	3810 (4)	6076 (3)	0·57	1·0
C(18)	5655 (6)	3995 (4)	5185 (3)	0·47	1·0
N(19)	1765 (5)	2206 (3)	3707 (2)	0·41	1·0
N(20)	2696 (4)	3268 (3)	4056 (2)	0·37	1·0
N(21)	8738 (5)	4098 (3)	3791 (2)	0·42	1·0
O(22)	9744 (7)	3824 (5)	4608 (3)	0·46	1·0
O(23)	7787 (7)	5070 (4)	3566 (3)	0·47	1·0
N(24)	4588 (5)	1968 (3)	969 (2)	0·39	1·0
O(25)	3524 (7)	2884 (4)	864 (3)	0·47	1·0
O(26)	4185 (7)	995 (5)	522 (3)	0·57	1·0
N(27)	942 (5)	431 (3)	2279 (2)	0·43	1·0
O(28)	595 (7)	9313 (4)	2272 (3)	0·57	1·0
O(29)	2401 (7)	882 (5)	2202 (3)	0·49	1·0
C(30)	9617 (7)	9587 (4)	4825 (3)	0·69	1·0
C(31)	8406 (7)	629 (4)	4623 (3)	0·64	1·0
C(32)	6518 (6)	433 (4)	4133 (3)	0·49	1·0
C(33)	5826 (6)	9237 (4)	3855 (3)	0·52	1·0
C(34)	7007 (6)	8190 (4)	4072 (3)	0·49	1·0
C(35)	8908 (7)	8357 (4)	4552 (3)	0·62	1·0
H(36)	5791 (13)	3801 (8)	2316 (6)	0·96	1·0
H(37)	7464 (14)	404 (7)	1183 (7)	1·01	1·0
H(38)	2412 (13)	5652 (8)	4633 (6)	1·01	1·0
H(39)	2029 (14)	7574 (7)	3600 (6)	1·15	1·0
H(40)	1932 (15)	7373 (8)	1893 (7)	1·26	1·0
H(41)	2174 (14)	5274 (9)	1183 (6)	1·22	1·0
H(42)	2480 (14)	3343 (8)	2211 (6)	1·13	1·0
H(43)	2907 (14)	1510 (9)	5386 (6)	1·30	1·0
H(44)	5472 (13)	1228 (8)	6931 (6)	1·04	1·0
H(45)	8106 (13)	2709 (8)	7383 (7)	1·08	1·0
H(46)	8295 (13)	4419 (8)	6260 (6)	1·09	1·0
H(47)	5715 (14)	4729 (9)	4694 (6)	1·21	1·0
H(48)	1086 (15)	9696 (10)	5178 (8)	1·64	1·0
H(49)	8973 (17)	1534 (9)	4842 (7)	1·66	1·0
H(50)	5576 (15)	1211 (9)	3982 (7)	1·47	1·0
H(51)	4340 (14)	9117 (8)	3495 (6)	1·22	1·0
H(52)	6505 (15)	7287 (9)	3857 (7)	1·49	1·0
H(53)	9831 (14)	7566 (8)	4714 (7)	1·18	1·0

Reflections were measured by scanning ω. The intensities of 1270 independent reflections were collected with $(\sin\theta)/\lambda < 0{\cdot}54$ Å^{-1} and $-7 < h < 7$, $-10 < k < 10$, $-14 < l < 14$; six reflections with negative intensity in the calculation *COLL5* were considered unobserved. A standard reflection, 080, showed 0·35% variation in intensity. Finally an absorption correction was applied to the data, with a linear coefficient $\mu = 1{\cdot}24$ cm^{-1}, corresponding to an incoherent cross section of H atoms taken as $\sigma = 40$ b for the wavelength of the experiment.

The positional parameters and anisotropic temperature factors of C, N, O and H nuclei were refined on F by the least-squares program of the *XRAY*76 system (Stewart, Machin, Dickinson, Ammon, Heck & Flack, 1976). The starting positions were those found by Williams at room temperature (Williams, 1967), the atomic numbering system being the same. The scattering lengths used in this refinement were $b_{\rm C} = 6{\cdot}65$, $b_{\rm N} = 9{\cdot}40$, $b_{\rm O} = 5{\cdot}80$ and $b_{\rm H} = -3{\cdot}74$ fm.

A $1/\sigma$ weighting scheme was applied to the reflections, where σ is the standard deviation of the experimental intensities. The final reliability factor was $R = (\sum\big|\,|kF_o| - |F_c|\,\big|)/\sum|kF_o| = 0{\cdot}032$, $(\Delta/\sigma)_{\max} = 0{\cdot}44$. The positional parameters and anisotropic temperature factors were refined. These positional parameters are displayed in Table 2 together with the isotropic equivalent temperature factors $B_{\rm eq}$. Atomic scattering lengths were from Bacon (1975); the secondary-extinction Larsen coefficient $g = 7{\cdot}90$ (32).

Finally, since it has been reported in the literature (Lothe & Eia, 1958; Krishnaji Misra, 1964) that the stoichiometry of benzene in the DPPH–C_6H_6 crystals may be less than unity, different refinements were

Table 3. *Bond distances* (Å) *and angles* (°)

	300 K(a)	10 K(b)		300 K(a)	10 K(b)		300 K(a)	10 K(b)
Central skeleton								
N(20)–N(19)	1·334 (6)	1·339 (4)	N(19)–C(1)	1·370 (6)	1·353 (4)	C(7)–N(20)–C(13)	121·3 (4)	121·1 (3)
N(20)–C(7)	1·422 (7)	1·440 (5)	N(19)–N(20)–C(7)	121·8 (4)	121·7 (3)	C(1)–N(19)–N(20)	118·5 (4)	119·0 (3)
N(20)–C(13)	1·419 (6)	1·418 (4)	N(19)–N(20)–C(13)	115·1 (4)	116·2 (3)			
Picryl ring								
C(1)–C(2)	1·420 (7)	1·435 (6)	C(6)–N(27)	1·471 (7)	1·483 (5)	C(2)–N(21)–O(23)	117·2 (6)	116·9 (3)
C(2)–C(3)	1·366 (7)	1·388 (5)	N(27)–O(28)	1·205 (6)	1·212 (5)	O(22)–N(21)–O(23)	124·2 (6)	125·7 (4)
C(3)–C(4)	1·389 (8)	1·399 (5)	N(27)–O(29)	1·217 (7)	1·242 (6)	C(4)–N(24)–O(25)	117·4 (6)	117·8 (3)
C(4)–C(5)	1·384 (8)	1·386 (6)	C(3)–H(36)	—	1·073 (10)	C(4)–N(24)–O(26)	118·1 (6)	118·2 (3)
C(5)–C(6)	1·370 (7)	1·385 (5)	C(5)–H(37)	—	1·071 (9)	O(25)–N(24)–O(26)	124·5 (6)	124·0 (4)
C(6)–C(1)	1·412 (7)	1·406 (5)	C(1)–C(2)–C(3)	123·1 (5)	123·2 (3)	C(6)–N(27)–O(28)	117·1 (6)	118·0 (4)
C(2)–N(21)	1·463 (7)	1·465 (5)	C(2)–C(3)–C(4)	119·2 (5)	118·3 (4)	C(6)–N(27)–O(29)	117·7 (6)	117·0 (3)
N(21)–O(22)	1·232 (6)	1·225 (5)	C(3)–C(4)–C(5)	121·2 (5)	122·3 (3)	O(28)–N(27)–O(29)	125·1 (6)	124·9 (4)
N(21)–O(23)	1·216 (6)	1·240 (5)	C(4)–C(5)–C(6)	117·8 (5)	116·6 (3)	C(2)–C(3)–H(36)	—	119·4 (5)
C(4)–N(24)	1·452 (7)	1·459 (5)	C(5)–C(6)–C(1)	124·7 (5)	126·1 (4)	C(4)–C(3)–H(36)	—	122·3 (5)
N(24)–O(25)	1·236 (7)	1·240 (6)	C(6)–C(1)–C(2)	113·9 (4)	113·3 (3)	C(4)–C(5)–H(37)	—	121·6 (6)
N(24)–O(26)	1·217 (7)	1·204 (5)	C(2)–N(21)–O(22)	118·5 (5)	117·2 (3)	C(6)–C(5)–H(37)	—	121·7 (6)
Phenyl C(7)								
C(7)–C(8)	1·373 (7)	1·380 (5)	C(11)–H(41)	—	1·086 (10)	C(9)–C(8)–H(38)	—	120·1 (6)
C(8)–C(9)	1·380 (8)	1·408 (5)	C(12)–H(42)	—	1·067 (10)	C(8)–C(9)–H(39)	—	119·5 (4)
C(9)–C(10)	1·370 (9)	1·387 (5)	C(12)–C(7)–C(8)	120·2 (6)	122·1 (4)	C(10)–C(9)–H(39)	—	120·1 (6)
C(10)–C(11)	1·378 (9)	1·409 (6)	C(7)–C(8)–C(9)	119·9 (6)	118·8 (4)	C(9)–C(10)–H(40)	—	119·6 (6)
C(11)–C(12)	1·382 (8)	1·397 (6)	C(8)–C(9)–C(10)	120·7 (6)	120·5 (4)	C(11)–C(10)–H(40)	—	120·6 (7)
C(12)–C(7)	1·405 (7)	1·405 (6)	C(9)–C(10)–C(11)	119·7 (6)	119·8 (4)	C(10)–C(11)–H(41)	—	119·1 (6)
C(8)–H(38)	—	1·086 (9)	C(10)–C(11)–C(12)	120·9 (6)	120·4 (4)	C(12)–C(11)–H(41)	—	120·5 (6)
C(9)–H(39)	—	1·097 (9)	C(11)–C(12)–C(17)	118·6 (6)	118·3 (4)	C(11)–C(12)–H(42)	—	121·1 (6)
C(10)–H(40)	—	1·072 (9)	C(7)–C(8)–H(38)	—	121·1 (6)	C(7)–C(12)–H(42)	—	120·6 (6)
Phenyl C(13)								
C(13)–C(14)	1·369 (8)	1·420 (6)	C(17)–H(46)	—	1·081 (10)	C(15)–C(14)–H(43)	—	121·0 (6)
C(14)–C(15)	1·383 (8)	1·405 (5)	C(18)–H(47)	—	1·066 (10)	C(14)–C(15)–H(44)	—	119·0 (6)
C(15)–C(16)	1·375 (10)	1·402 (6)	C(18)–C(13)–C(14)	121·2 (5)	122·1 (3)	C(16)–C(15)–H(44)	—	119·4 (6)
C(16)–C(17)	1·379 (10)	1·384 (6)	C(13)–C(14)–C(15)	119·7 (6)	117·6 (4)	C(15)–C(16)–H(45)	—	119·0 (6)
C(17)–C(18)	1·403 (8)	1·415 (5)	C(14)–C(15)–C(16)	120·9 (7)	121·5 (4)	C(17)–C(16)–H(45)	—	121·6 (7)
C(18)–C(13)	1·393 (8)	1·404 (6)	C(15)–C(16)–C(17)	119·4 (6)	119·4 (3)	C(16)–C(17)–H(46)	—	119·0 (5)
C(14)–H(43)	—	1·055 (11)	C(16)–C(17)–C(18)	120·9 (6)	121·8 (4)	C(18)–C(17)–H(46)	—	119·2 (6)
C(15)–H(44)	—	1·090 (10)	C(17)–C(18)–C(13)	117·9 (6)	117·6 (4)	C(17)–C(18)–H(47)	—	122·0 (6)
C(16)–H(45)	—	1·076 (9)	C(13)–C(14)–H(43)	—	121·4 (6)	C(13)–C(18)–H(47)	—	120·4 (6)
Benzene								
C(30)–C(31)	1·348 (13)	1·406 (6)	C(34)–H(52)	—	1·040 (10)	C(30)–C(31)–H(49)	—	118·2 (7)
C(31)–C(32)	1·382 (11)	1·397 (6)	C(35)–H(53)	—	1·069 (10)	C(32)–C(31)–H(49)	—	122·8 (7)
C(32)–C(33)	1·338 (11)	1·381 (6)	C(35)–C(30)–C(31)	119·7 (9)	119·9 (4)	C(31)–C(32)–H(50)	—	120·0 (6)
C(33)–C(34)	1·298 (11)	1·397 (6)	C(30)–C(31)–C(32)	119·5 (9)	119·0 (4)	C(33)–C(32)–H(50)	—	118·7 (6)
C(34)–C(35)	1·343 (13)	1·400 (6)	C(31)–C(32)–C(33)	118·1 (8)	121·2 (4)	C(32)–C(33)–H(51)	—	119·2 (6)
C(35)–C(30)	1·331 (13)	1·418 (6)	C(32)–C(33)–C(34)	121·5 (8)	119·9 (4)	C(34)–C(33)–H(51)	—	120·5 (6)
C(30)–H(48)	—	1·075 (11)	C(33)–C(34)–C(35)	121·1 (10)	120·3 (4)	C(33)–C(34)–H(52)	—	121·0 (7)
C(31)–H(49)	—	1·057 (11)	C(34)–C(35)–C(30)	119·9 (10)	119·6 (4)	C(35)–C(34)–H(52)	—	119·1 (7)
C(32)–H(50)	—	1·068 (11)	C(35)–C(30)–H(48)	—	118·4 (7)	C(34)–C(35)–H(53)	—	120·7 (6)
C(33)–H(51)	—	1·089 (6)	C(31)–C(30)–H(48)	—	121·6 (7)	C(30)–C(35)–H(53)	—	119·7 (6)

References: (*a*) Williams (1967), (*b*) this work.

carried out where this stoichiometry was slightly changed. The best agreement was obtained with the exact composition DPPH–C_6H_6, which implies that no benzene has evaporated.

Discussion. The shape of the molecule, with the thermal ellipsoids at 10 K, is shown in Fig. 1. The bond lengths and planar angles with their estimated standard deviations are given in Table 3, together with those determined by Williams (1967) at 300 K. The dihedral angles between the most important planes of the DPPH molecules are given in Table 4.

All the features of the conformation of DPPH at room temperature discussed by Williams are still valid at 10 K. The molecule is built around a central, non-planar, hydrazyl skeleton made up of atoms C(7), C(13), N(20), N(19) and C(1). The configuration around N(20) deviates only slightly from planarity, N(20) being 0·076 Å above the plane C(7), C(13), N(19) (0·081 Å at room temperature). The planes of the two central N atoms, defined as N(20), N(19), C(1) on the one hand and the least-squares plane of C(7), C(13), N(20), N(19) on the other hand, make an angle of 27·8° (28·5° at room temperature), and the C(1), N(19), N(20) bond angle becomes 119·0° (118·5° at room temperature).

The two phenyl rings are tilted unequally with respect to the mean N(20) plane: 48·6° for phenyl C(7) against 20·6° for phenyl C(13). The picryl ring is also tilted with respect to the N(20), N(19), C(1) plane, with an angle of 33·5°.

The four rings of the structure, including the interstitial molecule, are planar. The deviations from the best least-squares planes are listed in Table 5. The H atoms bonded to these rings are also in the planes. This is not the case for the N atoms of the picryl group except N(24) in the *para* position.

The bond distances determined by neutrons at 10 K are very close to those found with X-rays at room temperature, except for the C—C distances of the benzene molecule. We found at low temperature an average distance of 1·40 Å, while Williams' refinement at 300 K corresponds to 1·34 Å. Our average distance, 1·40 Å, is equivalent to the C—C distances in the three other rings. This distance agrees well with the distance usually accepted for the C—C bond in benzene (1·397 Å) (Pauling, 1967) and the distances determined by neutrons in solid benzene at low temperature (1·39–1·40 Å) (Bacon, Curry & Wilson, 1964). The apparent contraction of the free benzene molecule at room temperature is probably the result of the libration of this molecule, which is strong at 300 K but reduced at low temperatures.

On the other hand the C—H bond distances vary between 1·05 and 1·09 Å as expected [1·06–1·09 Å in solid C_6H_6 (Bacon *et al.*, 1964)] and the CCH angles are, within 2°, all equal to the theoretical value 120°.

Table 4. *Dihedral angles* (°) *between planes*

First plane	Second plane	300 K	10 K
Mean C(7)C(13)N(20)N(19)	N(20)N(19)C(1)	28·5	27·8
C(7)N(20)C(13)	N(20)N(19)C(1)	29·6	28·9
Mean C(7)C(13)N(20)N(19)	Mean phenyl C(7)	48·7	48·6
C(7)N(20)C(13)	Mean phenyl C(7)	54·3	53·8
Mean C(7)C(13)N(20)N(19)	Mean phenyl C(13)	21·6	20·6
C(7)N(20)C(13)	Mean phenyl C(13)	15·6	14·8
N(20)N(19)C(1)	Mean picryl	32·9	33·5
Mean C(2)N(21)O(22)O(23)	Mean picryl	32·5	32·9
Mean C(4)N(24)O(25)O(26)	Mean picryl	13·3	12·5
Mean C(6)N(27)O(28)O(29)	Mean picryl	54·2	53·2

Table 5. *Deviations* (Å) *from the best least-squares planes*

	300 K	10 K		300 K	10 K
Picryl					
C(1)	−0·011	0·000			
C(2)	0·024	0·021	N(21)	0·284	0·259
C(3)	−0·013	−0·020	H(36)	—	−0·040
C(4)	−0·009	0·001	N(24)	0·003	0·010
C(5)	0·019	0·018	H(37)	—	0·024
C(6)	−0·011	−0·022	N(27)	−0·125	−0·149
Phenyl C(7)					
C(7)	−0·003	−0·003			
C(8)	0·005	0·010	H(38)	—	0·018
C(9)	−0·003	−0·007	H(39)	—	−0·002
C(10)	−0·002	−0·002	H(40)	—	0·005
C(11)	0·004	0·009	H(41)	—	0·005
C(12)	−0·002	−0·007	H(42)	—	−0·031
Phenyl C(13)					
C(13)	0·001	0·005			
C(14)	0·004	0·000	H(43)	—	−0·018
C(15)	−0·006	−0·008	H(44)	—	−0·033
C(16)	0·004	0·010	H(45)	—	0·011
C(17)	0·000	−0·004	H(46)	—	−0·047
C(18)	−0·003	−0·004	H(47)	—	0·027
Benzene					
C(30)	−0·019	−0·008	H(48)	—	−0·036
C(31)	0·015	0·008	H(49)	—	0·012
C(32)	−0·003	0·001	H(50)	—	0·025
C(33)	−0·002	−0·009	H(51)	—	0·017
C(34)	−0·006	0·008	H(52)	—	−0·013
C(35)	0·015	0·000	H(53)	—	0·000

In conclusion, the low-temperature structure refinement of the DPPH–C_6H_6 crystal form by neutron diffraction confirms the previous X-ray determination and provides in addition the positional parameters of the H atoms together with the temperature factors at low temperature. This determination makes possible an accurate determination of the spin density over all the DPPH molecule by polarized neutron diffraction (Boucherle, Gillon, Maruani & Schweizer, 1987).

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Structure of a Novel Diels–Alder Adduct Derived from a Thebaine Analogue

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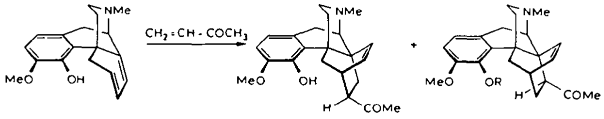
Abstract. (+)-8β-Acetyl-3-methoxy-17-methyl-4-phenoxy-6β,14β-ethenomorphinan, $C_{28}H_{31}NO_3$, $M_r = 429\cdot6$, orthorhombic, $P2_12_12_1$, $a = 7\cdot194\,(2)$, $b = 15\cdot511\,(3)$, $c = 20\cdot543\,(4)$ Å, $V = 2292\cdot3$ Å^3, $Z = 4$, $D_x = 1\cdot25$ g cm^{-3}, $\lambda(\text{Mo } K\alpha) = 0\cdot71069$ Å, $\mu = 0\cdot87$ cm^{-1}, $F(000) = 920$, $T = 293$ K, $R = 0\cdot045$ for 2582 observed $[I > \sigma(I)]$ reflections. The Diels–Alder reaction of (−)-6-demethoxy-β-dihydrothebaine with methyl vinyl ketone gives, besides a recently reported adduct, a second isomer with the acetyl group in the 8β position of the 6β,14β-ethenomorphinan skeleton. This means that both adducts result from addition of the dienophile from the α face of the morphinan-6,8-diene system, with the acetyl substituent directed towards the etheno bridge. There are no unusual bond lengths or angles.

Introduction. Recently, a simple, high-yield synthesis of 6-demethoxy-β-dihydrothebaine (1) was developed (Linders, Adriaansens, Lie & Maat, 1986). This compound undergoes almost quantitatively Diels–Alder reaction with methyl vinyl ketone yielding, besides the earlier reported adduct (2) (~ 60%) (van Koningsveld, Lie & Maat, 1984), a second isomer (3) (~ 35%). In principle, eight isomeric Diels–Alder adducts are possible starting from the morphinan-6,8-diene (1). The fragment peak m/z 57 [$C^+H{=}C(OH)CH_3$] in the mass spectrum of the second adduct (3) can be explained by a McLafferty rearrangement which is only possible in four isomers, namely the 7α-acetyl- and 8β-acetyl-6β,14β-ethenomorphinan and the 7β-acetyl- and 8α-acetyl-6α,14α-ethenoisomorphinan. The chemical shifts of the vinylic protons of the etheno bridge {δ 6–6·5 [m, 2H, H(18) and H(19)]} rule out the latter two ethenoisomorphinans [similar compounds show δ values lower than 6 for the signals of H(18) and H(19)]. The *endo* rule for Diels–Alder additions predicts the formation of the 8β-acetyl compound. However, unambiguous proof for the structure of (3) could neither be obtained from the mass spectrum nor from the ^{1}H NMR spectrum. Therefore, a single-crystal X-ray analysis was undertaken. A stable, well crystallizing derivative was obtained when the 4-hydroxyl substituent of (3) was converted into the phenyl ether by means of an Ullmann reaction with bromobenzene. The X-ray analysis confirmed the structure of (4) to be 8β-acetyl-3-methoxy-17-methyl-4-phenoxy-6β,14β-ethenomorphinan.



(1)
6-Demethoxy-β-dihydrothebaine

(2)

(3) $R = H$
(4) $R = C_6H_5$

Experimental. Title compound prepared in the Laboratory of Organic Chemistry, Delft, starting from 6-demethoxy-β-dihydrothebaine with methyl vinyl ketone. Crystals grown from diethyl ether, m.p. 403–404 K, $[\alpha]_D^{25\cdot0\,°C} = +90°$[chloroform/ethanol 9:1,

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