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2,2-Di-(4-*tert*-octylphenyl)-1-picrylhydrazyl as an Alkane-Soluble Standard for Electron Paramagnetic Resonance Studies

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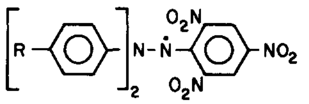
The title compound, a "waxy DPPH," was synthesized in three steps from *p,p'*-di-*tert*-octyldiphenylamine. The new radical showed spectral properties that were nearly identical to those of 2,2-diphenyl-1-picrylhydrazyl (DPPH), and it easily dissolved in all organic solvents tested except fluorolube and ethylene glycol. The radical was monomeric at −95°C in isooctane at a concentration of 0.4 m*M*.

2,2-Diphenyl-1-picrylhydrazyl (DPPH), 1a) is a very stable, persistent free radical first synthesized by Goldschmidt (*1*).



1a. R = H–
b. R = $(CH_3)_3CCH_2C(CH_3)_2$–

The attractive properties of DPPH have inspired numerous studies of the radical with EPR (*2*), NMR (*3*), ENDOR (*4*), electron-nuclear triple resonance (*5*), microwave-acoustic spectroscopy (*6*), and other techniques. The radical also has been widely used as a standard for measurement of g values (*7*) and of spin concentrations in static and kinetic EPR experiments (*8–11*).

For determination of spin concentrations, the use of solutions of DPPH is attractive because the ESR signal is broad and easily integrated. The intense purple color of the radical provides a qualitative visual indication of its presence. The radical is nonvolatile, unlike several commercially available dialkyl nitroxides which are sometimes also used for standardization. The disadvantages of DPPH are its limited solubility in paraffinic solvents, its slow rate of solution, and a tendency to crystallize in complexes with many solvents and also with occluded 2,2-diphenyl-1-picrylhydrazine (*8*). All of these disadvantages could be overcome with a suitable derivative. A methylated DPPH (**1**, R = CH_3) has been prepared (*12*) but did not analyze correctly, and has been reported to be unstable in the solid state (*13*). Balaban *et al.* (*14*) prepared 2,2-di-(3,5-di-*tert*-butylphenyl)-1-picrylhydrazyl in solution, but they apparently did not attempt to isolate the radical.

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In this paper we describe the synthesis of a tertiary alkyl derivative of DPPH which shows a number of rather satisfactory properties. The synthesis was adapted from published procedures (*1*, *14*, *15*).

EXPERIMENTAL

Instrumentation

Infrared spectra were recorded with a Perkin–Elmer 235B spectrophotometer, uv-visible spectra with a Perkin–Elmer Lambda-3 instrument, ^{1}H NMR spectra with a Varian EM-360 instrument, and ESR spectra with a Varian E104A spectrometer with the field set at 3242 G. Melting points were obtained from a Melt-Temp apparatus and are uncorrected. Microanalyses were performed by the Analytical Services Laboratory at Michigan Technological University and by Spang Microanalytical Laboratory.

Materials

4,4′-Di-*tert*-octyldiphenylamine (Vanlub 81) was obtained from R. T. Vanderbilt Company and was recrystallized from methanol/benzene before use. The purified product showed mp 99 to 101.5°C. Commercial-grade zinc powder was activated prior to use with concentrated HCl. All other reagents and solvents were used without further purification.

4,4′-Di-tert-octyldiphenylnitrosoamine. A solution of 4,4′-di-*tert*-octyldiphenylamine (10.0 g, 25.4 mmol) in 250 ml of 2-propanol and 2.5 ml concentrated HCl was treated at 0 to 5°C with stirring, with sodium nitrite (1.75 g, 25.4 mmol) dissolved in 2.5 ml H_2O and 5 ml ethanol. After 1 hour at 0 to 5°C the mixture was diluted with 75 ml H_2O. The precipitated light yellow nitrosoamine (9.00 g) was filtered off, washed with 2-propanol, and dried. A second crop (0.66 g) was obtained by reducing the filtrate to half-volume *in vacuo* and cooling in ice. Yield 9.66 g (90%), mp 64.5 to 65.5°C (from methanol). *Anal.* Calcd. for $C_{28}H_{42}N_2O$: C, 79.57; H, 10.02; N, 6.63. Found: C, 79.59; H, 9.67, N, 6.89%. Infrared(melt): 2950 vs, 2900 s, 1600 w, 1515 s, 1480 vs, 1410 w, 1400 w, 1370 s, 1320 w, 1260 w, 1210 w, 1180 s, 1100 w, 1050 s, 990 w, 950 w, 840 s, 560 vs, 680 w cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 7.00 to 7.67(m, 8H), 1.75(s, 4H), 1.40(s, 12H), 0.78(s, 18H). CAUTION: This nitrosoamine, like other compounds of this class, may be a carcinogen or a mutagen.

2,2-Di-(4-tert-octylphenyl)picrylhydrazine. The nitrosoamine (5.00 g, 11.8 mmol) in 75 ml of 2-propanol with 7.7 g (118.0 mmol) of activated zinc powder was treated dropwise with 15 ml acetic acid at 20 to 25°C during 0.25 hour with efficient stirring. After shaking on a table shaker for 3.5 hours the mixture was filtered and the filtrate was combined with several 2-propanol washings. Excess acetic acid was removed by shaking with sodium bicarbonate followed by filtration. Since isolation of pure 1,1-di-(4-*tert*-octylphenyl) hydrazine proved difficult, the crude material was converted without delay to the picrylhydrazine. The 2-propanol solution of 1,1-di-(4-*tert*-octylphenyl)hydrazine was treated with sodium bicarbonate (2.5 g, 29.8 mmol) and picryl chloride (3.3 g, 12.1 mmol). The brown mixture was refluxed for 0.5

hour and then stirred overnight at 25°C. Concentration *in vacuo* afforded a red-brown tar which was taken up in chloroform and washed with aqueous $NaHCO_3$ (3 × 50 ml). The chloroform solution was further washed with brine until the aqueous phase was nearly colorless. Removal of solvent *in vacuo* followed by crystallization from methanol/benzene (200 ml) afforded a first crop of fine red needles (4.90 g). A second crop was obtained from the filtrate (0.40 g). Yield 5.30 g (73%), mp 67°C dec. *Anal.* Calcd. for $C_{34}H_{45}N_5O_6$: C, 65.89; H, 7.32; N, 11.30. Found: C, 65.70; H, 7.28; N, 11.25%. Infrared(KBr): 3255 w, 2950 vs, 2870 sh, 1605 s, 1595 s, 1500 s, 1425 sh, 1330 vs, 1300 s, 1240 sh, 1170 w, 1085 w, 1020 w, 930 w, 840 w, 730 w, 600 w cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.50 to 6.93(m, 10H), 1.70(s, 4H), 1.33(s, 12H), 0.72(s, 18H).

2,2-Di-(4-tert-octylphenyl)-1-picrylhydrazyl. A chloroform (60 ml) solution of 2,2-di-(4-*tert*-octylphenyl)-1-picrylhydrazine (4.90 g, 7.91 mmol) was treated with lead dioxide (3.94 g, 16.5 mmol) and anhydrous sodium sulfate (3.17 g, 22.3 mmol). The mixture was mechanically shaken on a table shaker for 1 hour at 25°C. The resulting deep purple mixture was vacuum filtered through a fritted disc. Removal of solvent *in vacuo* afforded a dark purple oil. Fine purple needles resulted upon crystallization from methanol/ether. Yield 3.67 g (74%), mp 170 to 171°C. *Anal.* Calcd. for $C_{34}H_{44}N_5O_6$: C, 66.00; H, 7.17; N, 11.32. Found: C, 66.04; H, 7.08; N, 11.39%. Infrared(KBr): 2950 s, 1600 s, 1530 s, 1325 vs, 1260 w, 1220 w, 1170 w, 1080 w, 1020 w, 920 w, 840 w, 725 w, 615 w cm^{-1}.

RESULTS

The new radical **1b** was obtained in analytical purity by a conventional synthesis from the substituted diphenylamine. The compound appears to be stable indefinitely at room temperature. It dissolves readily in common organic solvents, and also in perfluorooctane and acetic acid, was sparingly soluble in 2,2,2-trifluoroethanol, but insoluble in ethylene glycol and fluorolube.

TABLE 1

OPTICAL ABSORPTION DATA FOR RADICALS **1**

Radical	Solvent	λ_{max} (nm)	ϵ ($M^{-1}cm^{-1} \times 10^{-4}$)	Reference
1a	Benzene	525	1.19	[a]
1a	95% Ethanol	518.3	1.16	This work
		327.1	1.63	
1b	Isooctane	530.4	1.33	
		338.6	1.56	
1b	Benzene	539.7	1.26	
		347.0	1.48	
1b	95% Ethanol	539.8	1.22	
		347.0	1.55	

[a] J. A. LYONS and W. F. WATSON, *J. Polym. Sci.* **18**, 141 (1955).

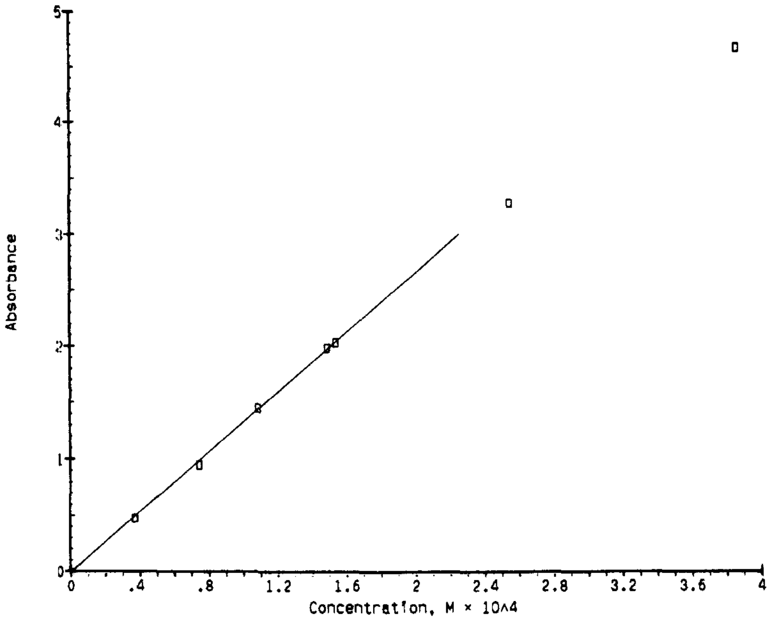

FIG. 1. Absorbance at 530 nm of **1b** as a function of concentration in isooctane. One value at $A = 2.0$ and the points at higher absorbances were obtained in a 0.1-cm cell and multiplied by 10.

The intense color of the radical is due to a transition at 530 to 540 nm which is analogous to the one which also appears in DPPH (Table 1). A plot of Beer's law in isooctane for this lower-energy maximum showed a progressive deviation from linearity above about 0.2 m*M* (Fig. 1).

The electron spin resonance spectrum of "waxy DPPH" in isooctane showed a signal with $g = 2.0$ and splitting into a distorted quintet (average $a_N = 9$ G) due to two slightly nonequivalent nitrogen atoms. Under specific conditions given in Fig. 2, additional splitting due to protons was just visible in degassed solutions. The spectrum appears entirely analogous to the spectrum of the 3,5-di-*tert*-butyl derivative which showed an average 9 G splitting (*14*), and is also consistent with the spectrum of the 4,4′-dimethyl derivative with reported a_N values of 7.6 and 9.8 G (*16*).

A plot of doubly integrated ESR response vs concentration (Fig. 3) was linear in the same concentration range as that used for the plot of Beer's law. If the points at lowest concentration were omitted, analysis of the remaining data by least-squares treatment gave a slope of 1.0052 ($r = 0.9998$).

When a solution of **1b** (0.2 m*M* is isooctane) was progressively cooled from 25° to −95° C the ESR signal broadened slightly and increased in overall intensity. The doubly integrated ratio of signals between these two temperatures showed an increase of 1.74, compared with a factor of 1.67 expected from the Boltzman factor. The solution remained intensely purple at the lower temperature and showed no evidence of crystallization.

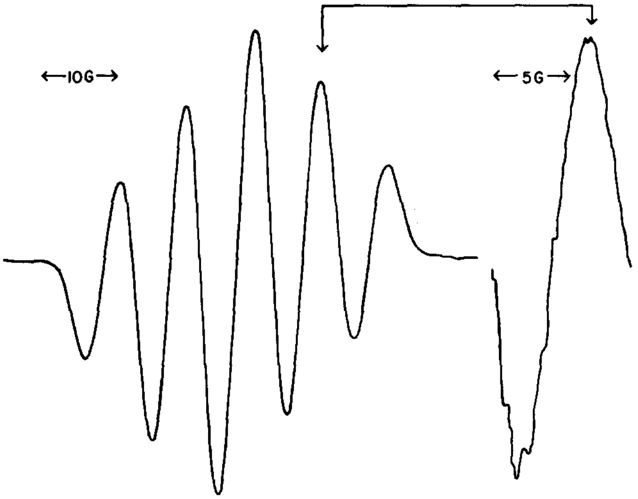

FIG. 2. Electron spin resonance spectrum of **1b** (approximately 10^{-4} M in degassed isooctane, microwave power = 0.6 mW, modulation amplitude = 200 G). The inserted spectral fragment showing fine structure was obtained with 5.95×10^{-5} M **1b** with a modulation amplitude of 0.08 G.

DISCUSSION

The new radical appears to have all of the desirable physical properties of the parent DPPH, and, in spite of a melting point about 40 degrees higher, it dissolves

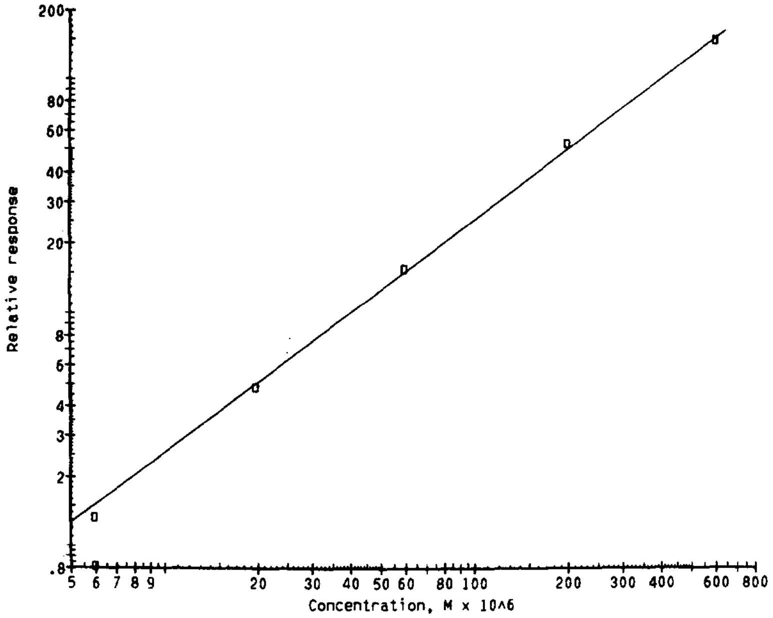

FIG. 3. Plot of the doubly integrated ESR signal of **1b** as a function of concentration in isooctane at 25°C.

easily in a wide range of solvents. The absence of dimerization of **1b** is indicated by the linearity of the spin plot at high concentrations, and by the normal ESR signal increase upon cooling a solution in isooctane. Since the parent DPPH is monomeric, it is not at all surprising that the substituted derivative should be also, particularly if dimerization were to occur by N–C bond formation at a *para* aromatic carbon analogous to the dimerization of triphenylmethyl (*17*). It was important to demonstrate this point for **1b**, however, if the radical were to be used for calibration of solutions at low temperatures.

The spin plot (Fig. 3) shows apparent deviation from linearity at a concentration of 6 μM. Although the signal at this concentration was noisy, the deviation is significant and probably represents a loss of radical by some adventitious reactions. In this context we should mention the observation that when a small amount of **1b** was dissolved in an unpurified, commercial sample of 2-methylbutane, the solution rapidly changed from purple to red-brown. Several workers have studied the reduction of DPPH to the corresponding hydrazine with reagents that include phenolic antioxidants (*18*, *19*).

The deviation of the optical density of **1b** from Beer's law (Fig. 1) is accompanied neither by a shift in λ_{max} nor (qualitatively) by a change in shape of the absorption envelope. Since the spin plot does not show a similar deviation in the same range of concentrations, there may be some sort of molecular association present which does not result in spin pairing.

The values of λ_{max} for **1b** are red-shifted about 20 nm compared with DPPH, which is similar to a corresponding shift of 16 nm reported by Walter (*20*) for the visible maximum of the *p*-methyl derivative in acetonitrile. The spectral parameters of **1a** and **1b** in ethanol do not differ substantially from the values in other solvents. A previous measurement (*21*) of the extinction coefficient of **1a** in ethanol is apparently in error.

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