

Factors affecting the Stability and Equilibria of Free Radicals. Part 11.¹ 1-Benzoyl-2,2-bis-(3,5-di-*t*-butylphenyl)hydrazyl and Its Temperature-dependent Electron Spin Resonance Spectrum

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The title free radical was prepared by oxidizing the corresponding hydrazine with lead tetra-acetate in benzene or toluene. Its e.s.r. spectrum undergoes reversible changes in the temperature range -90 to $+60$ °C. Simulated e.s.r. spectra indicate that the two di-*t*-butylphenyl groups are non-equivalent owing to restricted rotation around the N–N bond at low temperatures, but at 60 °C these two aryl groups become equivalent. The ΔG^\ddagger value of the rotation barrier is about 31 kJ mol^{-1} in the temperature range -30 to $+50$ °C.

Previous papers^{2–5} have reported the exceptional stability (persistence) of capto-dative (push–pull) aminyls, and in particular of hydrazyls (1) and (2) with acceptor groups R such as polynitrophenyl (1b, c),⁶ arylsulphonyl (1d),⁷ (2d),⁸ or cyano (1e),⁹ (2e).¹ 1,1-Diphenyl-2-picrylhydrazyl (DPPH) (1a)¹⁰ belongs to this class of compound, as does 1-benzoyl-2,2-diphenylhydrazyl (1f).^{11–13}

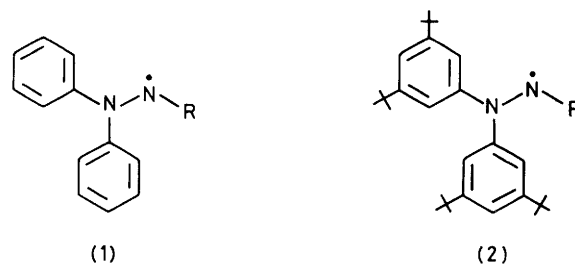
Reviews on hydrazyls^{14–16} and aminyls^{14,15,17} have been published. The push–pull aminyls (reviewed¹⁸) have been shown to be members of the larger class of capto-dative¹⁹ or mero-stabilized²⁰ free radicals (including carbon free-radicals). Theoretical treatments of the stabilization brought about by push–pull substituents in the latter radicals disagree. Some data predict^{21,22} and other calculations fail to find mero-stabilization in carbon free-radicals.²³ Calculations on aminyl systems (nitrogen free-radicals) with push–pull substituents are in progress.

In previous Parts we reported that the two aryl groups in (1) and (2) give rise to unequal hyperfine coupling constants (h.f.c.) thus providing evidence for restricted rotation around the N–N bond at room temperature [in (1d),⁷ (2d),⁸ (1e),⁹ and (2e)¹]. This observation is in agreement both with Linnett's theory²⁴ illustrated by formula (3), and with recent careful determinations of proton h.f.c.s in DPPH (1a) using deuterium labelling, ENDOR, and TRIPLE (electron–nuclear–nuclear magnetic resonance).²⁵

The four *t*-butyl groups in (2) simplify markedly the e.s.r. spectra relative to (1) by suppressing the small h.f.c.s due to the *meta*-protons (actually, these small couplings are replaced by even smaller couplings to the *t*-butyl protons but these are lower than the half-widths under normal e.s.r. measurement conditions). Previous investigations by Goldschmidt and Bader,¹¹ and by Wilmarth and Schwartz^{12,13} of the equilibrium between (1f) and its tetrazane dimer have used either optical methods or the reaction of (1f) with NO; e.s.r. spectra of (1f) are poorly resolved and too complicated for good simulation.²⁶ We therefore prepared the free radical (2f) and investigated its e.s.r. spectrum over a range of temperatures. This paper does not discuss the dissociation equilibrium between (2f) and its dimer, concentrating instead on the e.s.r. spectrum of the monomeric radical.

Experimental

E.s.r. spectra were recorded with a JEOL JES-ME-3X instrument in deaerated toluene using special vials described earlier.²



- a; R = 2,4,6-(NO₂)₃C₆H₂
- b; R = 2,6-(NO₂)₂C₆H₃
- c; R = 2,4-(NO₂)₂C₆H₃
- d; R = ArSO₂
- e; R = CN
- f; R = PhCO

Preparation of 1-Benzoyl-2,2-bis-(3,5-di-*t*-butylphenyl)hydrazine.—1,1-Bis-(3,5-di-*t*-butylphenyl)hydrazine^{1,8} (0.8 g, 2 mmol) was dissolved in benzene (10 ml) and this solution was added dropwise during 5 min to a stirred mixture of freshly distilled benzoyl chloride (0.275 g, 2 mmol) and sodium hydroxide (84 mg, 2 mmol) in water (3 ml). After stirring for 1 h, the organic layer was separated, dried, and concentrated to 5 ml under reduced pressure. On addition of light petroleum, the title hydrazine crystallised, m.p. (crude) 290° . Further purification from benzene–light petroleum raised the m.p. to 295° (hot stage) (Found: C, 82.1; H, 9.4; N, 5.5. C₃₅H₄₈N₂O requires C, 82.0; H, 9.4; N, 5.45%), δ (CDCl₃) 1.25 (36 H, s, Bu^t), 7.05 (6 H, s, *o*- and *p*-H), 7.3–7.9 (5 H, m, PhCO), and 8.10 (1 H, s, NH); ν_{max} (KBr) 3 269s (ν NH), 2 977vs, 2 909m, 2 871m (ν CH sat.), 1 662vs (amide), 1 592vs (arom.), 1 531m, 1 490m, 1 485m, 1 460–1 440 (unresolved), 1 392w, 1 366m, 1 340s, 1 320w, 1 295m, 1 250m, 1 205w, 920w, 859m, 729m, 718m, 699m, and 650w cm⁻¹.

Oxidation of this hydrazine to the hydrazyl (2f) in deaerated benzene or toluene was carried out as described earlier² using either lead dioxide or lead tetra-acetate.

Results and Discussion

1-Benzoyl-2,2-bis-(3,5-di-*t*-butylphenyl)hydrazine was prepared from benzoyl chloride and the corresponding 1,1-

diarylhydrazine. Its i.r. and ^1H n.m.r. spectra agree with the structure. Oxidation with lead dioxide or lead tetra-acetate in non-degassed benzene yields a solution with an unresolved e.s.r. spectrum with five components having intensities in the ratio 1 : 2 : 3 : 2 : 1 indicating coupling to two nitrogen atoms with approximately equal h.f.c.s. In deaerated toluene at room temperature, well resolved e.s.r. spectra were obtained.

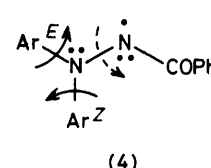
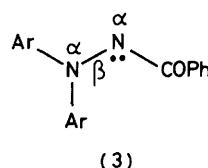
Literature data^{26,27} seem to indicate that the benzoyl group does not contribute with discernible h.f.c.s to the e.s.r. spectrum of (1f): indeed, (1f) and its *m*- and *p*-nitrobenzoyl derivatives were reported to afford practically identical e.s.r. spectra, suggesting that the carbonyl group insulates the aryl group (or, in other words, the coupling constants of the nuclei in the aryl group are lower than the line half-width). Only one report²⁶ mentions that the *o*-nitro-group in the *o*-nitrobenzoyl derivative of (1f) affects the e.s.r. spectrum; however, through-space coupling may be involved. In our case there is no substituent on the benzoyl group. Therefore, we will not include any coupling constant for the benzoyl protons in (2f).

An interesting observation is that the e.s.r. spectrum of (2f) undergoes marked and reversible changes on varying the temperature (Figure). At room temperature and above, the spectrum has 27 lines grouped in five 1 : 2 : 3 : 2 : 1 partly overlapping submultiplets (components) with seven lines each. At lower temperatures the lines of the marginal components become gradually broader and additional splittings become visible in the other components. All these changes are reversible and there is no intensity reduction over periods of several hours.

Tentative simulation with 'static' parameters shows that the spectrum at 60° can be simulated with six equal proton h.f.c.s and two slightly different a_N values (actually, the proton coupling constants are unequal but are averaged by rapid rotation around the N-N bond when the exchange time approaches zero). At lower temperatures the apparent 'static' proton h.f.c.s gradually diverge on decreasing the temperature into two sets of 3 a_H and 3 a'_H which reach constant values below -30 °C (their average value being the six equal h.f.c.s corresponding to 60 °C). This procedure enabled us to obtain the starting values for the matching of experimental and simulated spectra in terms of h.f.c.s which will be presented below.

The dramatic and reversible changes in the e.s.r. spectra of (2f) recorded at various temperatures from -90 to +60 °C indicate that in order to account for these changes the simulation must also include a dynamic parameter. We consider that rotation around the N-N bond [see formula (4), dotted line] is responsible for the temperature effect. As found by Biehl *et al.*²⁵ in DPPH (1a) this process has the highest rotation barrier, whereas rotations around N-aryl bonds [full lines in (4)] proceed much faster. Linnett's theory²⁴ indicates that the N-N bond ought to have a bond order of 1.5 according to formula (3) (where α and β indicate electrons with opposite spin). Calculations²⁸ also support the idea that the energy barrier for rotation around the N-N bond in hydrazyls could make this process observable in e.s.r. spectra at about room temperature.

We recorded the e.s.r. spectra of (2f) [*i.e.* (3 or 4; Ar = 3,5-Bu₂C₆H₃)] at the following temperatures: -90, -86, -76, -60, -49, -39, -30, -20, -10, 0, 10, 20, 30, 50, and 60 °C. Two slightly different nitrogen h.f.c.s (0.875 and 0.89 mT) were found to give the best agreement with the experimental spectra. The non-equivalence of the two aryl groups at low temperatures ought to lead to the partitioning of the six h.f.c.s into four sets: two *ortho* (*E*), one *para* (*E*), two *ortho* (*Z*), and one *para* (*Z*), but we find that satisfactory agreement can be obtained to an acceptable approximation



by a simpler model with only two sets of three h.f.c.s, neglecting the difference between *o*- and *p*- a_H values for the same aryl group. We assume one aryl group to have a_H 0.205 mT for its three *o*,*p*-protons, and the other aryl group to have a'_H 0.13 mT for its three *o*,*p*-protons.

To match the experimental e.s.r. spectra against calculated and simulated ones, we assume that rotations around the N-Ar bonds in (4) are immeasurably fast, and that the rotation around the N-N bond has an exchange time τ of the order 10^{-6} – 10^{-8} s in the temperature range -40 to +50 °C. One can thus simulate the experimental e.s.r. spectrum at 60 °C with $\tau = 0$, obtaining apparently equivalent aryl groups owing to fast rotation (Figure, top spectra): since the benzoyl group is found on the e.s.r. time-scale with equal probability close to Ar^E and Ar^Z, the six a_H values are averaged at this and higher temperatures. All line-widths L are equal under these conditions ($L = 1.96 \text{ MHz} = 0.07 \text{ mT}$).

From the theory of e.s.r. spectrometry it is known^{29,30} that the line-widths in e.s.r. spectra increase at the margins of the spectrum: if m is the quantum number of the component in the e.s.r. spectrum, then equation (1) holds where the

$$1/T_2 = A + Bm + Cm^2 \quad (1)$$

quadratic term Cm^2 makes the outer lines broader than the inner ones, and the linear term Bm causes asymmetric broadening, making the lines in the right-hand side of the spectrum broader than those on the left. Therefore in order to simulate the e.s.r. spectra satisfactorily at temperatures lower than 60 °C, we have to take into account different line-widths for the three components of the 1 : 2 : 3 : 2 : 1 multiplet: $m = 0$ (central, most intense, component, with the sharpest lines whose half-width remains constant over the whole range of temperatures), $m = \pm 2$ (outer, least intense, components with the broadest lines), and $m = \pm 1$ (intermediate components).

With these assumptions, by means of a specially devised computer program based on Lorentzian line shapes according to modified Bloch equations,³¹ it was possible to simulate satisfactorily all the e.s.r. spectra. In addition to the h.f.c.s mentioned above, this program makes use of two adjustable parameters: the exchange time τ and the half-width L . The Figure presents only two examples, with experimental and simulated data, for -10 °C (middle spectra; $\tau = 350 \text{ ps}$; for $m = \pm 2$, $L = 3.25 \text{ MHz} = 0.116 \text{ mT}$; for $m = \pm 1$, $L = 2.25 \text{ MHz} = 0.08 \text{ mT}$; for $m = 0$, $L = 1.96 \text{ MHz} = 0.007 \text{ mT}$) and for -30 °C (bottom spectra; $\tau = 600 \text{ ps}$; for $m = \pm 2$, $L = 5 \text{ MHz} = 0.178 \text{ mT}$; for $m = \pm 1$, $L = 2.5 \text{ MHz} = 0.089 \text{ mT}$; for $m = 0$, $L = 1.96 \text{ MHz} = 0.07 \text{ mT}$).

The free activation energy of the rotation, ΔG^\ddagger , was determined from Eyring's relationship, and the activation parameters ΔH^\ddagger and ΔS^\ddagger for the rotation around the N-N bond in (2f) were then obtained by plotting ΔG^\ddagger against the absolute temperature. Results are presented in the Table.

The value of *ca.* 31 kJ mol⁻¹ for ΔG^\ddagger is comparable with that of hindered internal rotation in terphenyl radical-ions which occurs over a comparable temperature range; since the terphenyl radical-ions have very complicated e.s.r. spectra, the analysis was performed by means of ENDOR.³² As already mentioned above, Biehl *et al.*²⁵ have determined the lowest

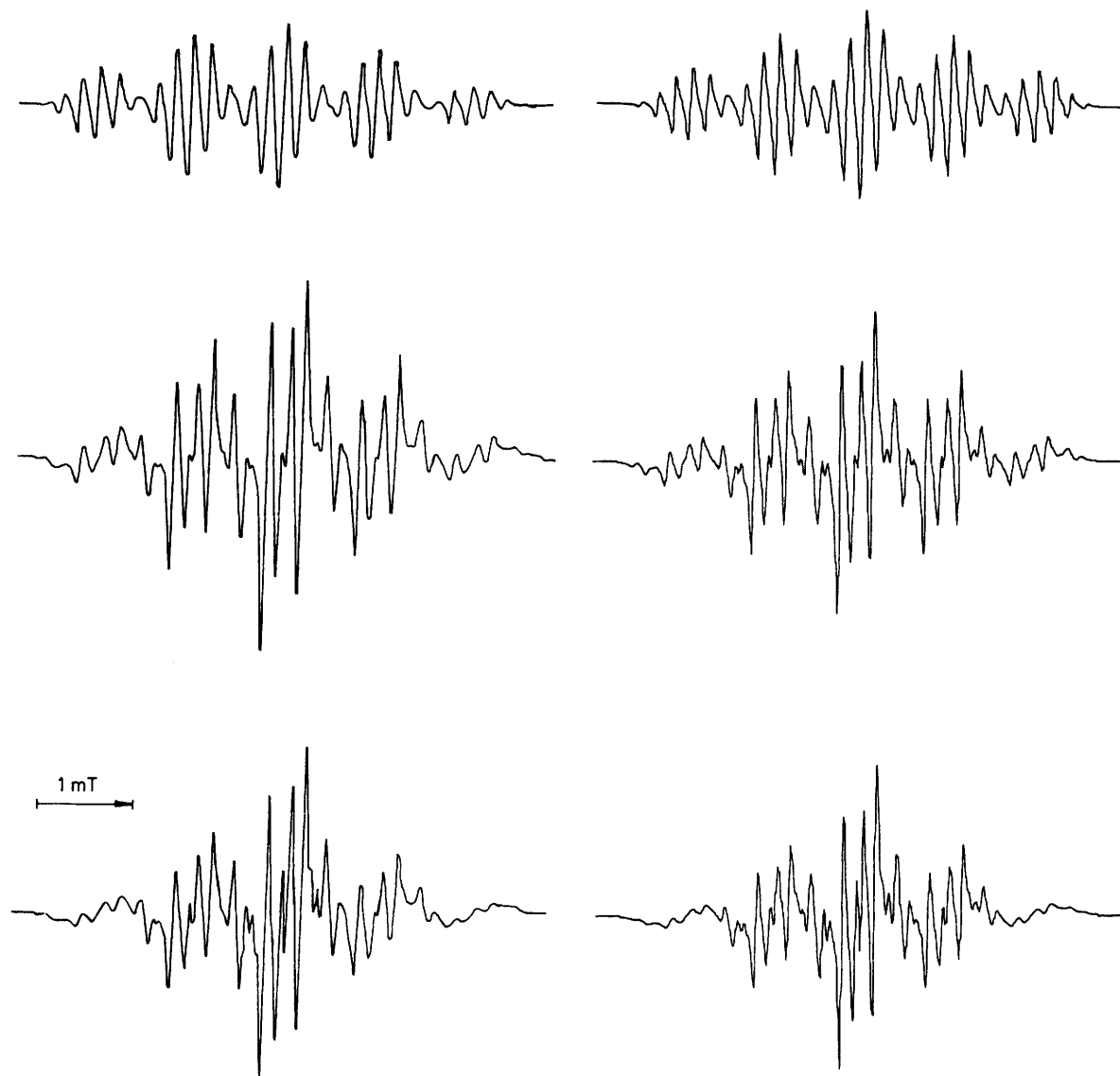


Figure. Experimental (left) and simulated (right) e.s.r. spectra of (2f) (60, top; -10, middle; and -30 °C, bottom)

Table. Variation of the exchange time τ versus temperature for radical (2f) in toluene, and activation parameters for rotation around the N-N bond [dotted line in formula (4)]

$t/^\circ\text{C}$	Exchange time τ/ps	$\Delta G^\ddagger/\text{kJ mol}^{-1}$
50	25	32.3
30	60	32.3
20	80	32.0
10	150	32.2
0	250	32.1
-10	350	31.6
-20	520	31.1
-30	600	30.1

From these data, the enthalpy and entropy of activation are ΔH^\ddagger 25.3 kJ mol⁻¹ and ΔS^\ddagger -23.1 J mol⁻¹ K⁻¹, respectively.

energy barriers for internal rotations of the phenyl and picryl groups of DPPH (1a) by using the ENDOR and TRIPLE methods. They could not reach temperatures where the rotation around the N-N bond proceeded observably on their time scale.

In our case, for radical (1f) we have determined the highest energy barrier for internal rotation around the N-N bond by simulating e.s.r. spectra by assuming exchange due to this rotation. This method complements those above,²⁵ and allows the determination of the rotation barrier for the first time in a hydrazyl. Since the non-equivalence of the aryl groups in hydrazyls (1) and (2) is a general phenomenon, future determinations of the rotation barriers around the N-N bond in other hydrazyls will elucidate the factors influencing these barriers, and will perhaps allow quantitative evaluation of the capto-dative effect from the barrier to internal rotation.

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