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FACTORS AFFECTING STABILITY AND EQUILIBRIA OF FREE RADICALS—XII[1]

CAPTO-DATIVE DIARYLAMINYLS WITH POLYNITROPHENYL AND 3,5-di-t-BUTYLPHENYL GROUPS

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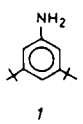
Abstract—The synthesis of 3,5-di-t-butylphenyl-polynitrophenylamines is reported, with 2,6-dinitro- and 2,4,6-trinitrophenyl groups. Oxidation converts these amines into capto-dative diarylaminyls which are stable in solution at room temperature. Their ESR spectra are described; simulation yields hyperfine coupling constants with lower values for the acceptor than for the donor group. This is the first time that the EST spectra of aminyls with polynitrophenyl groups are amenable to satisfactory simulation.

A previous paper in this series[2] has reported enhanced persistence of diarylaminyls when one of the aryl groups is an electron donor and the other an electron acceptor (push–pull,[2] or capto-dative[4] aminyls). This phenomenon has also been called merostabilization[5] and has theoretical backing.[6–8] Relevant literature references were reviewed earlier[9] or more recently.[10]

Along with electronic stabilizing factors, steric shielding around the aminyl N also contributes to the extraordinary persistence of such push–pull aminyls as diphenylpicrylhydrazyl (DPPH).[11–14]

The present paper reports two new diarylaminyls in which a weakly donor group (3,5-di-t-butylphenyl) is associated with a strong acceptor which causes also steric overcrowding around the aminyl N: 2,4,6-trinitrophenyl or 2,6-dinitrophenyl. The two di-t-Bu groups were introduced in order to suppress small *meta*-coupling constants and thus to lead to simpler ESR spectra, which can be interpreted by simulation affording meaningful hyperfine coupling constants. It should be stressed that so far no ESR spectra of radicals with polynitrophenyl groups have been amenable to simulation. The hyperfine coupling constants of DPPH were recently determined by Möbius *et al.* who used another method involving extensive D labelling in all various possible ways, and triple nuclear (^{1}H)- nuclear (^{2}H)-electronic resonance.[14]

Reaction of 3,5-di-t-butylaniline (**1**)[15,16] with 2,6-dinitrochlorobenzene afforded the 3,5-di-t-butyl-2',6'-dinitrodiphenylamine **2**. Reaction of **1** with picryl chloride yielded the 3,5-di-t-butyl-2',4',6'-tri-nitrodiphenylamine **3**.



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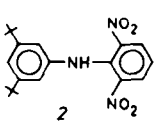

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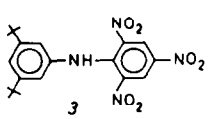


3

IR and ^{1}H NMR spectra (*cf* Experimental) confirm the structures of the reaction products.

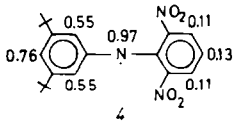
ESR spectra

Oxidation of each of the above two diarylamines **2** and **3** with lead tetraacetate or dioxide in benzene gave rise to stable solutions of capto-dative (push–pull) diarylaminyls **4** and **5**, respectively, which were conservable at room temperature and gave well resolved ESR spectra.

Figure 1 presents the ESR spectrum of the free radical **4** (top trace). Using a specially devised computer program, this ESR spectrum was simulated (bottom trace) with the following hyperfine coupling constants (hfc's): one a_N = 0.97 mT; one a_H = 0.76 mT; two a_H's = 0.55 mT; two a_H's = 0.11 mT; and one a_H = 0.13 mT. The half-width is 0.065 mT so that the shape of the ESR spectrum does not change markedly on varying the last hfc in the range 0.11–0.13 mT.

Figure 2 presents the ESR spectrum of the free radical **5** (top trace). By a similar procedure as that described above, the simulated spectrum (bottom trace) was obtained in terms of the following hfc's: one a_N = 0.977 mT, one a_H = 0.795 mT, two a_H's = 0.555 mT, and two a_H's = 0.11 mT. The half-width is, as in the previous case, 0.065 mT.

The formulas of **4** and **5** and the hfc's assigned to various nuclei are displayed.



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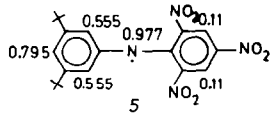

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Despite slight differences between the experimental and simulated ESR spectra, it is evident that the struc-

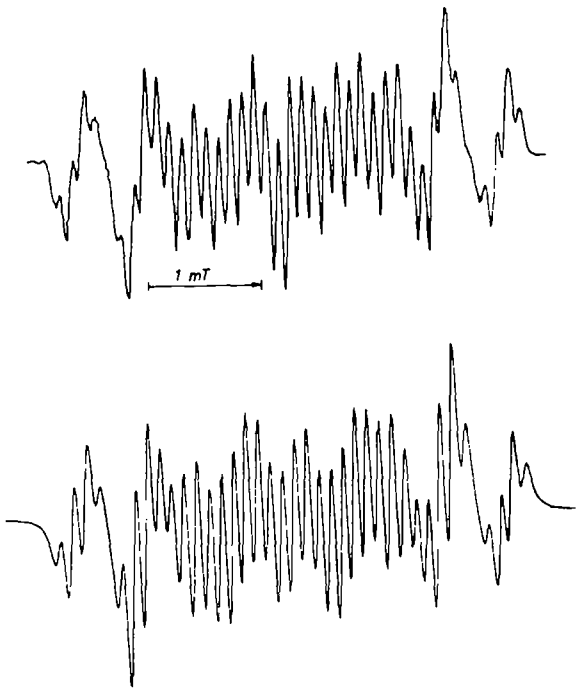


Fig. 1. ESR spectrum of 3,5-di-t-butylphenyl-2',6'-di-nitrophenyl-aminyl **4** in benzene (top trace) and simulated spectrum (bottom).

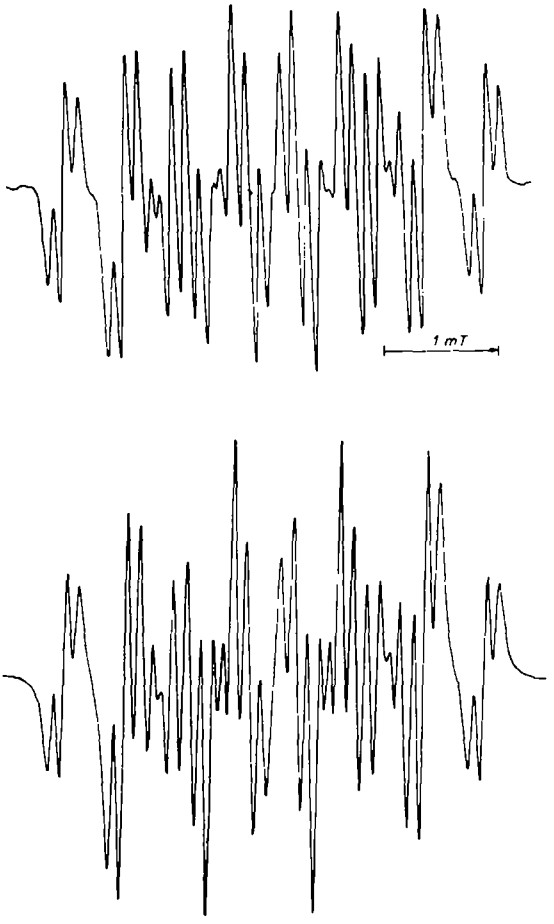


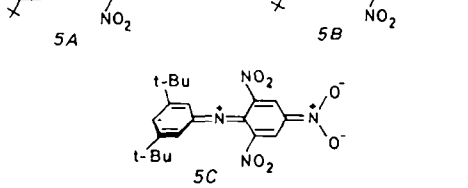
Fig. 2. ESR spectrum of 3,5-di-t-butylphenyl-picryl-aminyl **5** in benzene (top trace) and simulated (bottom).

ture of the radicals is in agreement with their mode of formation, and that no intramolecular ring closure involving the aminyl N and an *ortho*- standing NO_2 group has taken place; such a reaction would have led to a nitroxide and destroyed the symmetry of the polynitrophenyl group).

The above data for the coupling constants of **4** and **5** are in good agreement with the values determined by Miura *et al.*[15] for 3,5-di-t-butylphenyl-N-sulphonylaminyls: $a_N = 0.77–0.78$, $a_{o-H} = 0.56$; $a_{p-H} = 0.76$ mT.

Our data for the picryl amino group of **5** are also in good agreement with the hfc's of DPPH determined by Biehl *et al.*[14] using ENDOR: the *m*-protons in DPPH have $a_H = 0.106$ mT, the picrylamino N of DPPH has $a_N = 0.974$ mT, and the NO_2 groups have low negative hfc's $a_N = -0.048$ mT for the *p*-NO_2 group, and -0.039 mT for the *o*-NO_2 groups. The small hfc's of NO_2 groups (lower than the half-width) account for the fact that in ESR spectra their corresponding splittings are absent. A similar reason explains why under the given conditions the splitting due to the t-Bu protons cannot be observed.

The distribution of the unpaired spin density which is apparent from hfc's indicates that the donor group delocalizes more spin density than the acceptor group. This finding is in agreement with the qualitative reasoning which explains why donor aryl groups stabilize more strongly the symmetrically substituted diarylaminyls than acceptor aryl groups: whereas acceptor groups delocalize preferentially the unshared electron pair, the unpaired electron can be delocalized by both acceptor and donor groups. In capto–dative aminyls, the predominant limiting structures place most of the spin density on the donor group (*cf* **5A**) while the negative and of the dipole is situated on the acceptor group (*cf* **5B**). A



simultaneous delocalization of the unpaired electron on the donor group and of the unshared electron pair on the acceptor group (*cf* **5C**) is improbable because this would involve a different (sp) hybridization of the aminyl N, and perpendicular aryl rings. Actually, the a_N value of 0.97 mT indicates a π-radical **5** rather than a σ-radical **5B**.

EXPERIMENTAL

ESR spectra were recorded with a Jeol JES-ME-3X spectrometer, ^{1}H-NMR spectra with a Varian A-60A instrument, and IR spectra with a Jena-UR 20 spectrophotometer. Simulated spectra were calculated and plotted with a Hewlett–Packard computer. Melting points were determined with a Boetius hot state.

3,5-*Di-t-butylphenyl-2',6'-dinitrodiphenylamine* (**2**). A soln of 4.1 g (20 mmole) 3,5-di-t-butylaniline[16–18] and 2.0 g (10 mmoles) 2,6-dinitrochlorobenzene in 50 ml MeOH was refluxed for 5 hr. The soln was cooled at $-20°$ when long orange-red needles precipitated, which were filtered off (3.5 g, 94% yield), m.p. (crude) 128–131°. After recrystallization from MeOH the m.p. increased to 136–137°. Found: N, 11.50; $C_{20}H_{25}N_3O_4$ requires: N, 11.31%). IR (CS_2, CCl_4, cm^{-1}): 716 m, 725 m, 745 m, 885 m, 925 m, 1285 s, 1350 m, 1540 m, 1601 m, 1629 m, 2909 m, 2970 s, 3340 m. ^{1}H NMR ($CDCl_3$, δ-values, ppm): 1.25 (s, 18H, t-Bu), 6.88 (d, J = 1.8 Hz, 2H-2,6), 6.98 (t, J = 8.2 Hz, 1H-4'), 7.30 (t, J = 1.8 Hz, 1H-4), 8.30 (d, J = 8.2 Hz, 2H-3',5'), 9.78 (s, 1H, NH).

3,5-*Di-t-butylphenyl-2',4',6'-trinitrodiphenylamine* (**3**). A soln of 8.2 g (40 mmol) 3,5-di-t-butylaniline and 4.95 g (20 mmol) picryl chloride in 75 ml MeOH was refluxed for 5 hr. After cooling at $-10°$, red needles precipitated and were filtered off (8 g, 96.5% yield); m.p. 198.5–199.5° after recrystallization from MeOH. (Found: C, 57.90; H, 6.01; N, 13.54. $C_{20}H_{24}N_6O_6$ requires: C, 57.68; H, 5.81; N, 13.45%). IR (KBr, cm^{-1}): 719 m, 731 s, 742 m, 885 m, 930 m, 1000 m, 1180 m, 1290 vs, 1348 s, 1360 s, 1445 m, 1540 s, 1597 vs, 1631 s, 2878 w, 2918 w, 2970 s, 3109 m, 3346 s. ^{1}H NMR ($CDCl_3$, δ-values ppm): 1.31 (s, 18H, t-Bu), 6.91 (d, J = 1.8 Hz, 2H-2,6), 7.39 (t, J = 1.8 Hz, 1H-4), 913 (s, 2H-3',5'), 10.33 (s, 1H, NH).

Free radicals **4** and **5** were obtained by oxidizing the diarylamines **2** and **3**, respectively, with lead tetraacetate or with lead dioxide in deaerated benzene solution using special vials which were described in an earlier paper.[2]

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