[2,2]Paracyclophanyl-nitroxides

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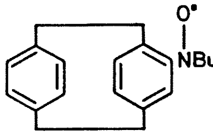
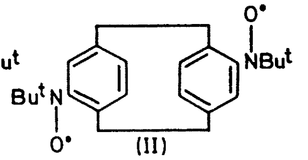
Summary The exceptionally stable t-butyl-4-[2,2]paracyclophanylnitroxide (I) and *NN'*-di-t-butyl[2,2]paracyclophan-4,16-diylbisnitroxide (II) have been prepared and their spectral properties examined.

THE existence of powerful transannular electronic effects in [2,2]paracyclophanes has been convincingly demonstrated in a number of ways.[1] In mono-substituted [2,2]paracyclophanes, however, transannular delocalisation of electronic charge, as indicated by valence-bond structures, does not correctly predict the structures of the isomers formed on electrophilic substitution. The bulk of the experimental results of Reich and Cram[2] indicate that "predominant substitution occurs pseudo-*gem* to the most basic positions of substituents in the already substituted ring." With a view to establishing whether a parallel situation exists in paracyclophanyl radicals we have begun a study of the spectral and chemical properties of paracyclophanyl nitroxides.

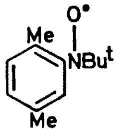
Treatment of 4-lithio[2,2]paracyclophane and pseudo-*p*-dilithio[2,2]paracyclophane in tetrahydrofuran with 2-methyl-2-nitrosopropane followed by aerial oxidation of the ensuing hydroxylamines yielded the extremely stable, crystalline nitroxides (I) and (II), respectively.



(I)



(II)



(III)

The nitrogen coupling constant (14·7G) obtained from the e.s.r. spectrum of the radical (I), like that of t-butyl-2,5-dimethylphenylnitroxide[3] (III) (13·5G), is larger than that of t-butylphenylnitroxide (12·3G) and clearly the nitroxide group is substantially twisted out of the "plane"[4] of the ring to which it is bonded. As a result, the proton hyperfine splittings are correspondingly smaller and cannot be satisfactorily resolved by e.s.r. measurements. However, the n.m.r. spectrum of (I) (see Figure 1), after comparison with that of (III) and related o-alkylaryl-t-butylnitroxides,[5] gave values for the Bu^t (−0·559G), *ortho* (−1·025G), *meta* (+0·309G) and *para* (−0·303G) protons. The values for the protons in the other ring cannot be unequivocally assigned at this stage but they are obviously much smaller than those quoted above, lying in the range +0·034 to −0·181G. The preparation of homologous radicals whose spectra will be of help in the further interpretation of the above spectrum is underway.

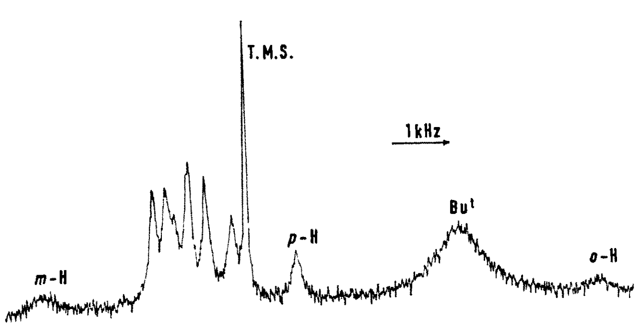


FIGURE 1. *N.m.r. spectrum of nitroxide* (I): 220 *MHz, in* CCl_4.

The e.s.r. spectrum of the bisnitroxide (II) (Figure 2) is remarkably similar to that of the biradical (IV) in which there is modulation of the exchange interaction (*J*) between the unpaired electrons, the average value of *J* being much larger than the nitrogen hyperfine coupling.[6] The modulation of *J* in (IV) has been attributed to intramolecular conformational changes which are a consequence of the flexibility of the group linking the two nitroxide ends. In our biradical (II), in which such motion is not possible, modulation of *J*, from which the alternating linewidth arises, could be due to rotational isomerism of the nitroxide groups (*cf.*, the radical-anion of dinitrodurene[7]) or to the relative movements of the two rings (concertina and twisting motions) previously investigated by Lonsdale and her co-workers.[8]

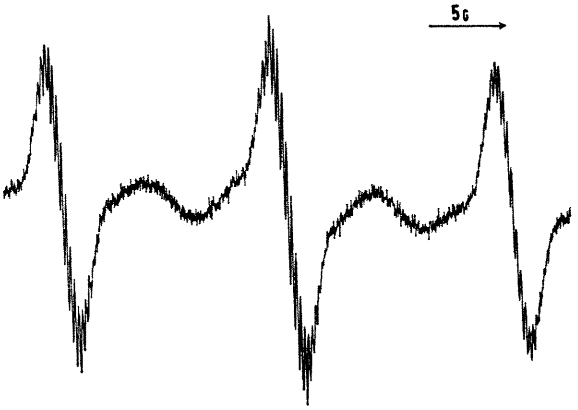
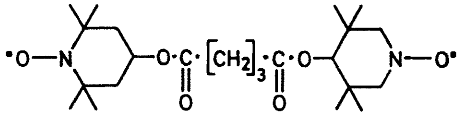


FIGURE 2. *E.s.r. spectrum of bisnitroxide* (II), *in* CCl_4.



(IV)

A small quantity of a purple product was also isolated during the preparation of the bisnitroxide (II). This we consider to be a t-butylamino-[2,2]paracyclophanequinone on the basis of mass measurement (*M*, 309·1732; $C_{20}H_{23}NO_2$ requires 309·1729), i.r. [3400 cm^{-1} (NH), 1655 cm^{-1} (CO)] and n.m.r. [τ 8·65 (Bu^tNH)] studies, and from its ease of reduction by dithionite. The presence of a charge-transfer band in its u.v. spectrum at shorter wavelength (326 nm) than that in the spectrum of the unsubstituted [2,2]paracyclophanequinone[9] (340 nm) suggests that the t-butylamino-group is in the quinone ring but this has still to be confirmed.

The formation of aminoquinones by the spontaneous decomposition of halogenoaryl-t-butylnitroxides has been observed previously.[10] In this case either pseudo-*p*-bromo-[2,2]paracyclophanyl-t-butylnitroxide or an isomer (resulting from the presence of a trace of another dibromo-isomer in our sample of pseudo-*p*-dibromo[2,2]paracyclophane) could be the source of the quinone.

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