

SOME MECHANISTIC CONSIDERATIONS OF HINDERED AMINE UV STABILISERS

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ABSTRACT

Hindered amines are good uv stabilisers. Tetra-substituted hindered amines are usually better uv stabilisers than tri-substituted ones. Among bicyclo tri-substituted amines the uv stabilisation activity appears to depend on the degree of hindrance around the nitrogen atom and the way in which the two rings are fused together.

This conclusion is based on the finding that 2,2,4-trimethyl-trans-decahydroquinoline (trans-TDQ) is a better uv stabiliser than cis-TDQ in polypropylene. The same trend was found between 1-(2-hydroxyethyl)-2,2,4-trimethyl-trans-decahydroquinoline (trans-HETDQ-1) and cis-HETDQ-1. The difference in the uv stabilisation activity of these isomers is explained in terms of the relative stability of the nitroxyl radical of trans and cis TDQ.

INTRODUCTION

The first patent on hindered amines as uv stabilisers for various plastics was issued to the Sanko Company in 1969.¹ Since then numerous patents and papers have been published. However, it was not until recently that reasonable mechanisms by which hindered amines protect various plastics from photodegradation and oxidation were revealed by various authors.²⁻⁹ Although the proposed mechanisms do not explain all the reasons why certain hindered amines are excellent uv stabilisers in polymers, the prevalent ideas appear to be as follows: the ability of nitroxyl radicals ($\text{>NO}\cdot$) to scavenge alkyl radicals ($\text{R}\cdot$) and that of alkyl ether (>NOR) to react with peroxy radicals ($\text{ROO}\cdot$) to stop chain propagation. These two steps appear to be feasible if stable nitroxyl radicals can be formed from hindered amines. The present paper reinforces the argument that a hindered amine with the ability of forming a more stable nitroxyl radical is a better uv stabiliser than an amine that forms a less stable one.

EXPERIMENTAL

Materials

2,2,4-Trimethyldecahydroquinoline (TDQ), 1-(2-hydroxyethyl)-2,2,4-trimethyldecahydroquinoline (HETDQ-1) and 1-(2-hydroxyethyl)-2,2,4,8-tetramethyldecahydroquinoline (HETDQ-2) were prepared as described in patents.^{10,11} 3,3-Dimethyl-*trans*-decahydroquinoxaline-2-one (DDQ) was supplied by Dr J. T. Lai. Bis-(2,2,6,6-tetramethyl-4-piperidiny) sebacate (Tinuvin 770), [2,2'-thio-bis(4-*tert*-octylphenolato)] *n*-butylamine nickel (Cyasorb 1084), distearyl thiodipropionate (DSTDP), tris(3,5-di-*tert*-butyl-4-hydroxybenzyl) isocyanurate (Goodrite 3114), 2,6-di-*tert*-butyl-*p*-cresol (CAO-1), cobalt dicyclohexyl dithiophosphate (Cyasorb 2548), 2,2-diphenyl-1-picrylhydrazyl (DPPH·), methylene blue, *p*-menthane hydroperoxide and rubrene are commercially available and were used without further purification. All the solvents were either spectral grade or distilled.

Structural formulae of some of these compounds are given in Table 1.

TABLE I

| Abbreviation | Chemical structure | Chemical name |
|----------------------------|--------------------|--|
| HETDQ-1 | | 1-(2-Hydroxyethyl)-2,2,4-trimethyldecahydroquinoline |
| HETDQ-2 | | 1-(2-Hydroxyethyl)-2,2,4,8-tetramethyldecahydroquinoline |
| DDQ | | 3,3-Dimethyl- <i>trans</i> -decahydroquinoxalin-2-one |
| Tinuvin 770 | | Bis(2,2,6,6-tetramethyl-4-piperidiny) sebacate |
| Dinitroxide of Tinuvin 770 | | Bis(2,2,6,6-tetramethyl-1-oxyl-4-piperidyl) sebacate |
| Cyasorb 1084 | | [2,2'-Thio-bis(4- <i>t</i> -octylphenolato)] <i>n</i> -butylamine nickel |
| Cyasorb 2548 | | Cobalt dicyclohexyldithiophosphate |

Apparatus

Ultra-violet and visible spectra were obtained on a Beckman spectrophotometer DK 2A. IR and ESR spectra were obtained on a Perkin-Elmer 467 spectrophotometer and a Varian E-3 ESR spectrometer, respectively.

Sargent thermonitor Model SW (Catalogue No. S-82055) was used as a constant temperature bath for the decomposition of alkylhydroperoxides.

(a) A general procedure for the singlet oxygen quenching experiment

In a 250-ml three-necked flask were placed 1×10^{-4} mole/litre or 1×10^{-3} mole/litre of a uv stabiliser, 100 ml of dry benzene and 100 ml of dry ethanol. To the above solution, magnetically stirred, were added 2 ml of methylene blue master solution (made from 0.662 g of methylene blue in 100 ml of dry benzene and 100 ml of dry ethanol) and 5 ml of rubrene master solution (made from 0.1103 g of rubrene in 25 ml dry benzene and 25 ml of dry ethanol). The first sample (about 4 ml) was withdrawn.

A stream of air (280 cc/min) was introduced into the reaction medium through a gas bubbler. Immediately, the reaction was irradiated with visible light from an Eastman Kodak Carousel 800 projector equipped with a 500 W quartz iodine lamp and a yellow filter (Corning Glass Work, 3387). Samples were withdrawn periodically and analysed for the concentration of rubrene left in the reaction mixture.

Since the visible spectrum was run in a 1 cm cell, the absorptivity of the rubrene solution at 525 nm was readily obtained by applying the equation:

$$a = \frac{A}{b \cdot c} = \frac{\text{Absorbance}}{(1 \text{ cm})(\text{concentration of rubrene g/litre})}$$

$$= \frac{\text{Absorbance}}{(0.05329 \text{ g/litre})(1 \text{ cm})}$$

to the original solution. Using this absorptivity value, the concentration of rubrene at various reaction intervals can be calculated.

(b) A general procedure for the alkylhydroperoxide decomposition experiments

A 0.0005 molar solution (250 ml) was prepared of a uv stabiliser or antioxidant in chlorobenzene (distilled and degassed). This solution was placed in a 500-ml three-necked flask which was, in turn, placed in a constant temperature bath at 95.0°C. As the temperature reached 95.0°C, 5 ml of CAO-1 master solution (50 ml of chlorobenzene solution containing 0.0020 g of CAO-1) and 5 ml of *p*-menthane hydroperoxide master solution (50 ml of chlorobenzene solution containing 1.640 g of *p*-menthane hydroperoxide) were added. The mixture was stirred for one minute and a 20 ml sample of the reaction mixture (time zero) was taken, cooled to room temperature and weighed to four significant figures. The amount of *p*-menthane hydroperoxide was measured by iodometric titration. Samples were similarly

withdrawn periodically and the concentration of *p*-menthane hydroperoxide remaining in the pot was measured.

(c) *A general procedure for the reaction of 2,2-diphenyl-1-picryl-hydrazyl (DPPH·) with various compounds*

In a 250-ml Erlenmeyer flask were placed 5.0×10^{-3} mole/litre of a uv stabiliser or antioxidant and 100 ml of dry benzene. The mixture was stirred and 5 ml of DPPH· master solution (0.1242 g of DPPH· in 50 ml of dry benzene) and 105 ml of dry benzene were added in one portion.

Immediately the first sample was withdrawn and the concentration of DPPH· was determined from its absorption at 512 nm. Additional samples were taken periodically and analysed in the same manner.

Synthesis of bis-(2,2,6,6-tetramethyl-1-oxy-4-piperidiny) sebacate: In a 500-ml Erlenmeyer flask were placed 12.0 g of bis-(2,2,6,6-tetramethyl-4-piperidiny) sebacate (Tinuvin 770), 0.75 g of Versene EDTA (Trilon B or tetra sodium salt of EDTA), 0.75 g of sodium tungstate, 165 ml of methanol and 50 ml of water. The mixture was stirred with cooling. Then 12.5 ml of 30% H_2O_2 was added over a period of five minutes. The pot temperature rose to 5°C. Five days later the resulting slurry was filtered to collect an orange solid which was recrystallised from hexane (melting point: 60–61°C).

Anal. Calcd. for $C_{28}H_{50}N_2O_6$: C, 65.85; H, 9.87; N, 5.48; O, 18.80.

Found: C, 66.15; H, 9.89; N, 5.44; O, 18.90.

Preparation of 2,2,4-trimethyldecahydroquinoline-1-oxy: Both 90% and 41% 2,2,4-trimethyl-*trans*-decahydroquinoline-1-oxy were prepared under the same conditions and in the same molar scale.

In a 500-ml Erlenmeyer flask were placed 18.1 g (0.1 mole) of 2,2,4-trimethyldecahydroquinoline (90% *trans*), 1.5 g of Trilon B, 1.5 g of sodium tungstate, 120 ml of methanol and 35 ml of water. To the above stirred and cooled ($-5^\circ C$) mixture were added 25 ml of 30% H_2O_2 over a period of 5 min. The solution

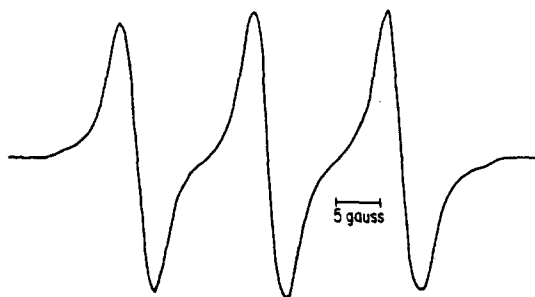


Fig. 1. ESR spectrum of 2,2,4-trimethyldecahydroquinolene-1-oxy (90% *trans*) in benzene.

was allowed to reach room temperature and to react for 5 days. Methanol was removed from the resulting yellow solution. The residue was extracted four times with ether and the ether solution washed six times with water. The ether layer was dried over anhydrous magnesium sulphate, filtered and concentrated. The resulting yellow syrup showed a strong band at 1370^{-1} cm which is ascribable to the nitroxyl group. It was further characterised by an ESR spectrum (see Figs 1 and 2).

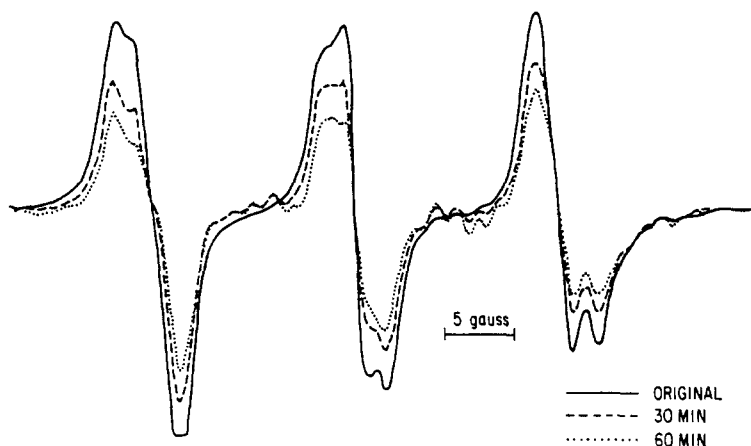


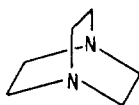
Fig. 2. ESR spectra of 2,2,4-trimethyldecahydroquinolene-1-oxyl (40% *trans*) in benzene.

Synthesis of bis-(1,2,4,6,6-pentamethyl-4-piperidiny) sebacate: In a 500-ml three-necked flask were placed 120.2 g (0.25 mole) of bis-(2,2,6,6-tetramethyl-4-piperidiny) sebacate (Tinuvin 770) and 17.5 g of paraformaldehyde. The mixture was heated and stirred. When the pot temperature reached 93°C , 33 g of formic acid (88%) was added dropwise over a period of 14 min. The pot temperature was maintained at $78\text{--}93^{\circ}\text{C}$ for five hours and cooled to an ambient temperature. The following morning a syrup was removed from the lumpy material and was distilled under reduced pressure. The fraction boiling at $224\text{--}8^{\circ}\text{C}/0.20$ mm Hg (boiling point: $218\text{--}220^{\circ}\text{C}/0.4$ mm Hg; British patent 1,399,239) was used for the singlet oxygen quenching experiment.

RESULTS AND DISCUSSION

(a) Quenching of singlet oxygen by uv stabilisers

In 1968 Quannes and Wilson¹² discovered that amines are efficient singlet oxygen quenchers. They showed that 1,4-diazabicyclo-[2.2.2] octane (1) is a powerful inhibitor of singlet oxygen reactions in solution and that (1) (DABCO) also quenches singlet oxygen in the gas phase.¹²

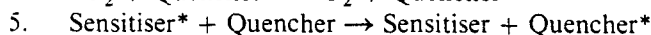
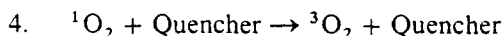
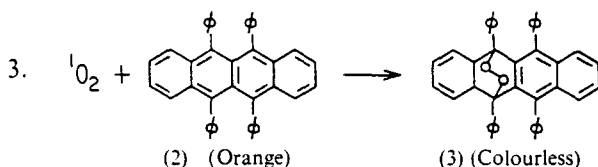
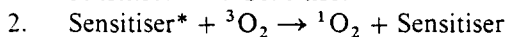
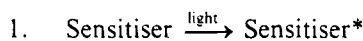


(1)

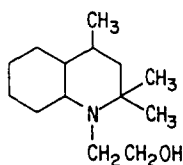
Since then, numerous papers have been published¹³ showing various amines as excellent singlet oxygen quenchers.

In the area of plastics, two papers reported that singlet oxygen is a reactive intermediate in the photo-oxidation of simple olefins¹⁴ as well as of polyethylene.¹⁵

With this background knowledge we undertook an investigation of the singlet oxygen quenching efficiency of hindered amines. Singlet oxygen was generated by using methylene blue as a sensitizer. The light source employed was an Eastman Kodak Carousel 800 projector equipped with a 500 W quartz iodine lamp and a filter (Corning glass work 3387).¹⁶ The relative singlet oxygen quenching efficiency of various amines and commercial uv stabilisers was measured by following the concentration of rubrene (2) ($\lambda_{\max} = 520 \text{ nm}$). In the absence of any quencher, rubrene would form a colourless *endo*-peroxide (3). In the presence of an efficient quencher, whether it is an amine or organometallic, reaction 4 would be much faster than reaction 3 and the concentration of rubrene would decrease slowly. On the other hand, in the presence of an inefficient quencher, reaction 3 would be expected to go much faster than reaction 4.



Using 1×10^{-2} mole/litre of 1-(2-hydroxyethyl)-2,2,4-trimethyldecahydroquinoline (4) as a quencher, rubrene was subjected to singlet oxygen. After only 4 min, less than half of the original concentration of rubrene remained in the reaction mixture.



(HETDQ-1)

(4)

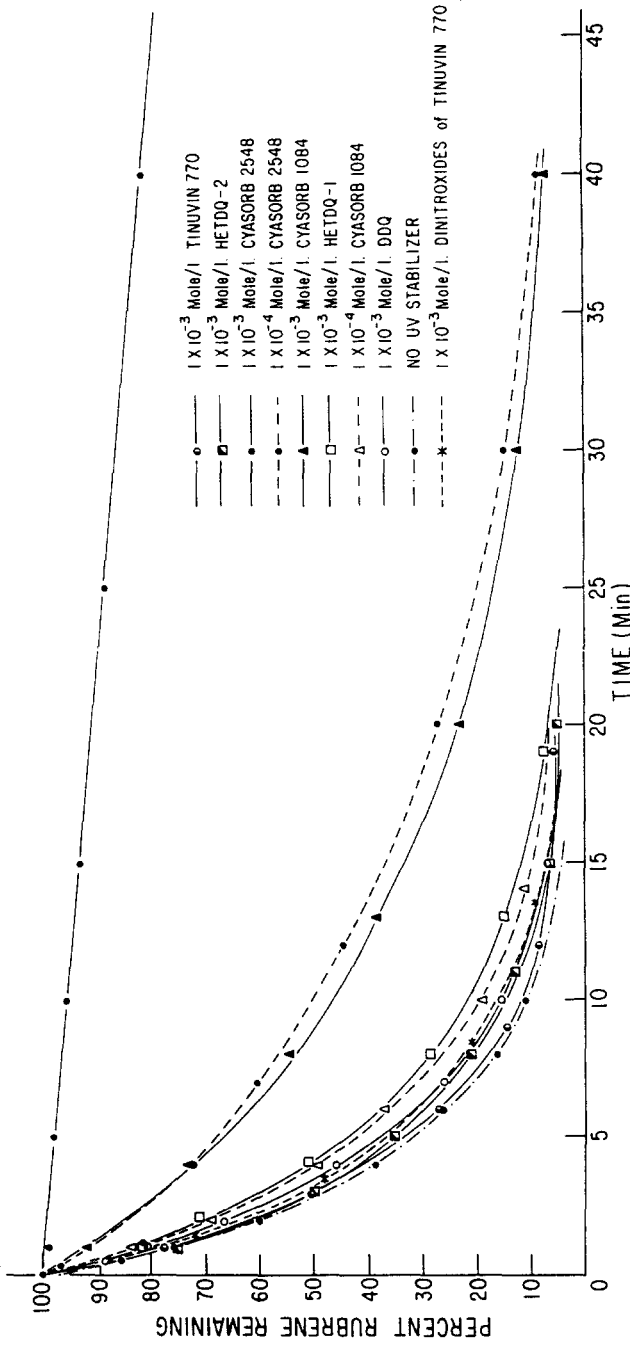


Fig. 3. Quenching of singlet oxygen by various uv stabilisers in the presence of rubrene.

In order to prevent the amine from quenching the activated sensitiser (reaction 5), its concentration was kept below $5 \times 10^{-3} \text{M}$.¹⁷ Results from four hindered amines, one nitroxyl radical and two organometallics are plotted in Fig. 3.

Somewhat surprisingly, all hindered amines were found to be poor singlet oxygen quenchers. These results are supported by the work recently published by Monroe and others.^{18(a)(b)(c)} On the other hand, the dinitroxide of Tinuvin 770 is a slightly better singlet oxygen quencher than its parent compound (Tinuvin 770), as shown in Fig. 3. Nevertheless, the difference between Tinuvin 770 and its dinitroxide as a singlet oxygen quencher is not great enough to explain the excellent uv stabilisation of Tinuvin 770. Better singlet oxygen quenchers are organometallics—Cyasorb 1084 and 2548—yet these are much less effective uv stabilisers than Tinuvin 770.

(b) *Decomposition of a hydroperoxide by hindered amines and a sulphur compound*

The detrimental effect of hydroperoxide in the photo-degradation of polypropylene is well documented by Carlson and Wiles.² In order to find out whether hindered amines play any role in the decomposition of hydroperoxide, *p*-menthane

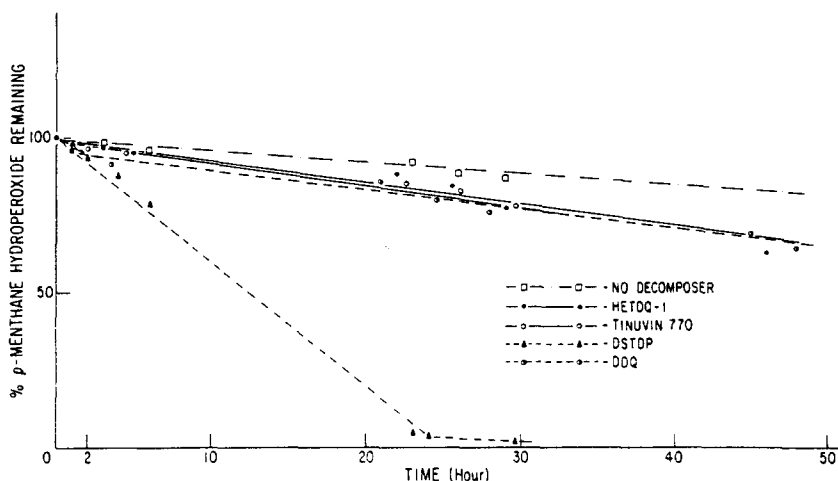


Fig. 4. Decomposition of *p*-menthane hydroperoxide in chlorobenzene at 95°C.

hydroperoxide was reacted with a hindered amine in chlorobenzene at 95°C. The concentration of the peroxide was determined by iodometric titration. The results were compared with the one from distearyl thiodipropionate (DSTDP). As shown in Fig. 4, DSTDP is a much superior hydroperoxide decomposer than three hindered amines (DDQ, HETDQ-1 and Tinuvin 770) we have investigated. Consequently, it is safe to conclude that hindered amines are not good hydroperoxide decomposers.

(c) Reaction of hindered amines with 2,2-diphenyl-1-picrylhydrazyl (DPPH·)

In order to determine whether hindered amines can donate a hydrogen atom, they were reacted with 2,2-diphenyl-1-picrylhydrazyl (DPPH·):

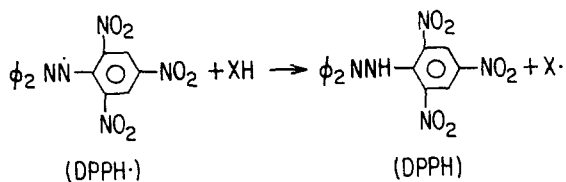


Figure 5 illustrates clearly that hindered amines do not donate a hydrogen atom as a hindered phenol does.

(d) Comparison of 2,2,4-trimethyl-trans-decahydroquinoline-1-oxyl (trans-TDQ-1-oxyl) and its cis isomer

While we were synthesising and evaluating derivatives of 2,2,4-trimethyldecahydroquinoline (TDQ) as uv stabilisers, it became apparent that TDQ with high *trans* isomer content was a better uv stabiliser for polypropylene than the *cis* isomer.

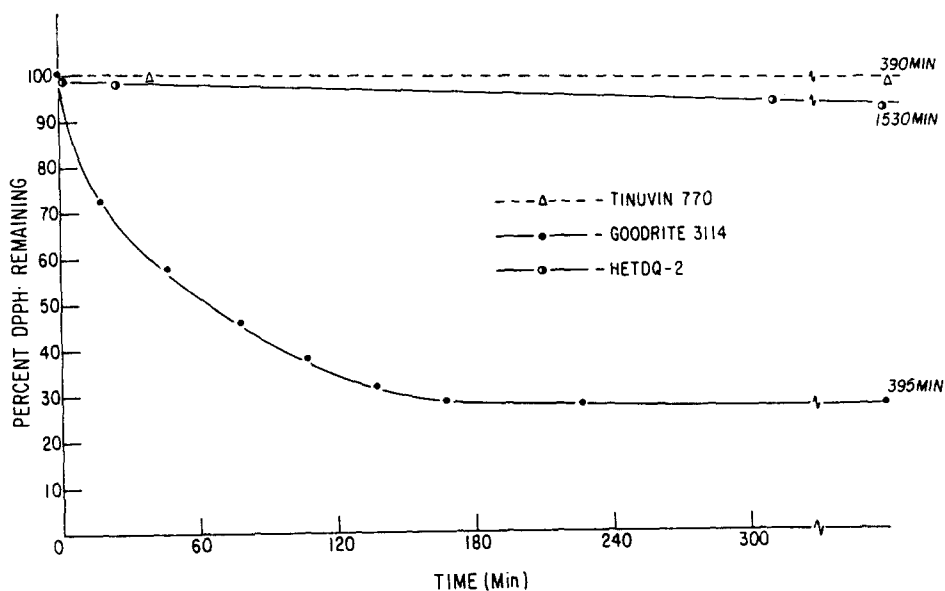
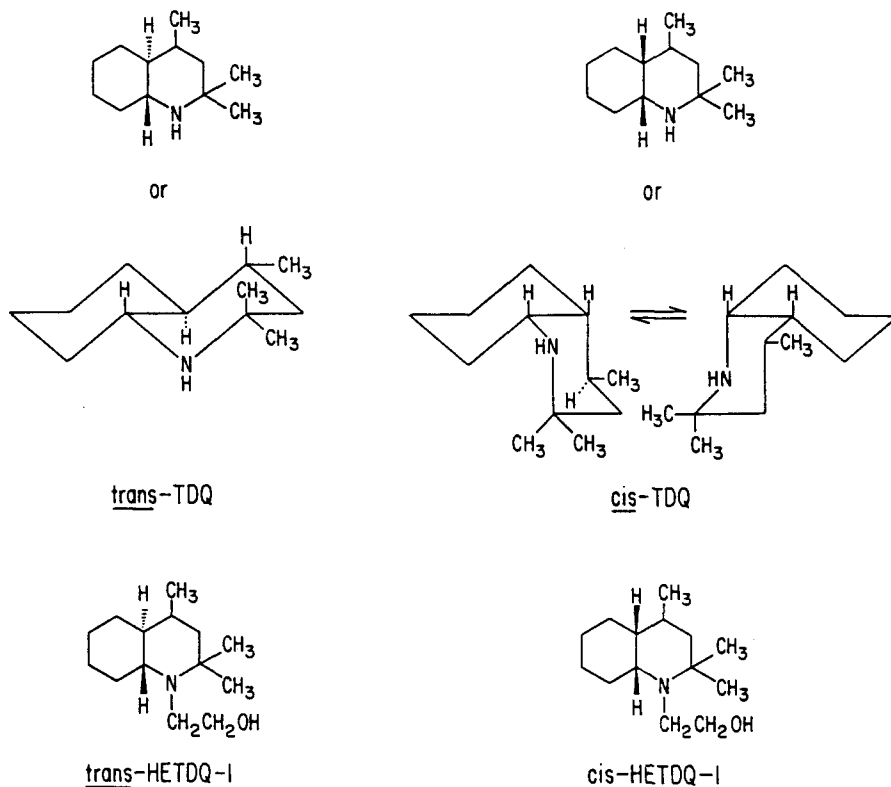


Fig. 5. Reaction of 2,2-diphenyl-1-picrylhydrazyl (DPPH·) with hindered amines.

(Since pure *cis* and *trans*-TDQ are not available, *trans*-TDQ implies that it has higher *trans* isomer content than *cis*-TDQ.)



The same phenomenon was also observed between 1-(2-hydroxyethyl)-2,2,4-trimethyl-*trans*-decahydroquinoline (*trans*-HETDQ-1) and *cis*-HETDQ-1 (see Table 2).

Using Rozantsev's method,¹⁹ 2,2,4-trimethyl-*trans*-decahydroquinoline-1-oxyl (*trans*-TDQ-1-oxyl) was prepared from *trans*-TDQ. Since we did not have pure *trans* and *cis* TDQ, we used TDQ with the highest and lowest *trans* isomer content available.



TABLE 2
XENON WEATHEROMETER DATA OF POLYPROPYLENE SAMPLES^a CONTAINING
VARIOUS UV STABILISERS

| Additive (0.5 phr) | Failure time (h) ^b | | |
|--|-------------------------------|--------|--------|
| | 2 mil | 20 mil | 30 mil |
| TDQ (85% <i>trans</i>) | — | 2580 | — |
| TDQ (96% <i>trans</i>) | — | 3050 | — |
| HETDQ-1 (58% <i>trans</i>) | 1610 | — | 1895 |
| HETDQ-1 (96% <i>trans</i>) | 2840 | — | 4065 |
| HETDQ-2 (96% <i>trans</i>) ^c | 3117 | — | 9811 |

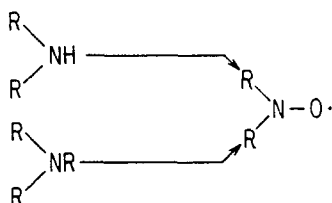
^a All samples contain 0.25 phr Irganox 1010.

^b They are based on carbonyl absorbance (1720 cm^{-1}).

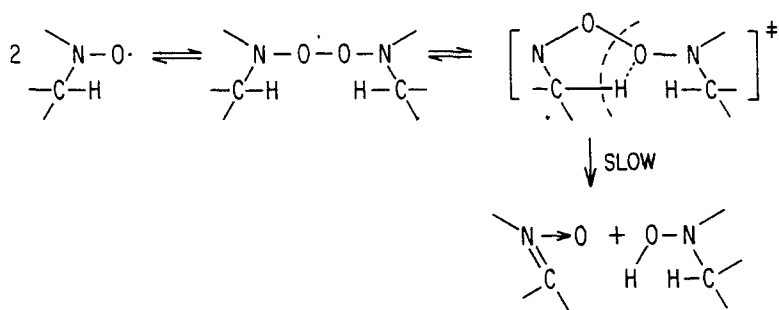
^c 1-(2-Hydroxyethyl)-2,2,4,8-tetramethyldecahydroquinoline.

Both nitroxyl radicals were prepared under the same conditions and characterised by IR and ESR spectroscopy (see Figs 1 and 2).

ESR spectroscopy also enables us to determine the stability of *trans*- and *cis*-TDQ-1-oxyl. As illustrated by Figs 1 and 2, the ESR spectrum of 2,2,4-trimethyldecahydroquinoline-1-oxyl (90% *trans*) remained constant for more than two days (after which we did not take additional ESR spectra). In contrast, 2,2,4-trimethyldecahydroquinoline-1-oxyl (40% *trans* or 60% *cis*) was unstable and the nitroxyl radical signal decreased rather rapidly (see Fig. 2). Thus, a correlation between a stable nitroxyl radical and a good uv stabiliser in polypropylene appears to exist. Since the oxidation of di- and tri-alkylamines with tertiary butyl peroxide is known to yield the same nitroxyl radicals,^{20,21} it is possible that *trans*-HETDQ-1 would also form a more stable *trans*-TDQ-1-oxyl in the presence of an alkylhydroperoxide. This explains why HETDQ-1 with high *trans* isomer content is a better uv stabiliser than the one with low *trans* isomer.



The question, then, is why *trans*-TDQ-1-oxyl is more stable than *cis*-TDQ-1-oxyl. It has been known for many years that those nitroxyl radicals with at least one α -hydrogen atom undergo a self-reaction to form a nitron and a hydroxylamine. Moreover, Bowman *et al.*²² have demonstrated that the reaction involves the reversible formation of a nitroxide dimer which undergoes slow decomposition to a hydroxylamine and a nitron.



If we accept Bowman *et al.*'s theory and build molecular models of *cis*- and *trans*-TDQ-1-oxyl dimers, then it becomes very clear why *cis*-TDQ-1-oxyl is less stable than *trans*-TDQ-1-oxyl. As shown in Fig. 6 (for the sake of clarity only a portion of TDQ-1-oxyl molecule is shown), H—C—N—O—O lies on the same plane, and O—O bond breakage and O—H bond formation are facilitated. On the other hand, the

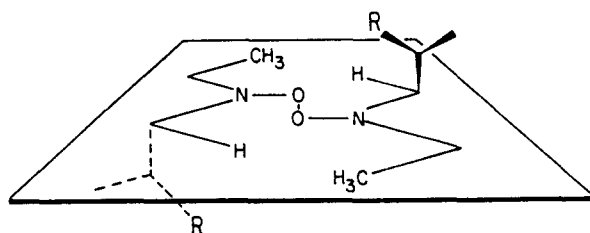


Fig. 6. A dimer of *cis*-TDQ-1-oxyl.

co-planarity of H—C—N—O—O is not possible for the dimer of *trans*-TDQ-1-oxyl, as shown in Fig. 7. Consequently, *trans*-TDQ-1-oxyl is more stable than *cis*-TDQ-1-oxyl. Extending the same line of argument, a methyl group at the 8 position makes the formation of a dimer of 2,2,4,8-tetramethyldecahydroquinoline-1-oxyl very difficult. This is reflected in the excellent photo-stabilisation property of HETDQ-2 (90% *trans*) (see Table 2). From these observations it is not difficult to explain why *tetra*-substituted hindered amines such as bis-(2,2,6,6-tetramethyl-4-piperidyl) sebacate (Tinuvin 770) are excellent uv stabilisers—they simply do not

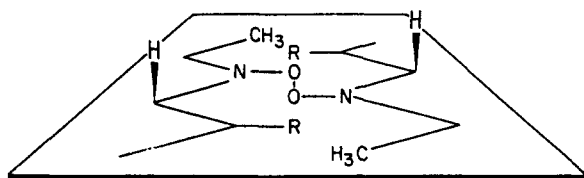
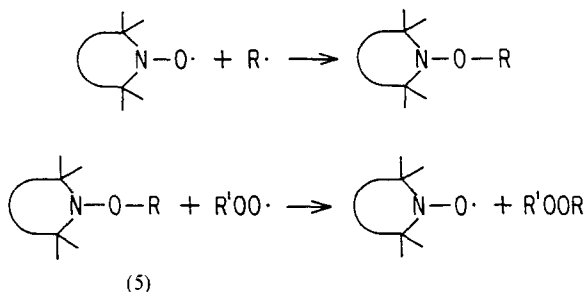


Fig. 7. A dimer of *trans*-TDQ-1-oxyl.

have an α -hydrogen atom to form a nitron and a hydroxylamine. The foregoing conclusions are based on the assumptions that the major product of the reaction of α -hydrogen atom-containing hindered amines with alkyl hydroperoxides, singlet oxygen, or uv light, is a nitroxyl radical and that the nitroxyl radical decomposes^{2,3} via its dimer into a nitron and a hydroxylamine.

The important role that a stable nitroxyl radical plays in the photo-stabilisation of polyolefins is well documented by Carlson and Wiles² and others.^{3,24} According to the prevailing theory, a stable nitroxyl radical can trap out an alkyl radical ($R\cdot$), forming an ether (5).



Compound (5) can react in turn with a peroxy radical to regenerate a nitroxyl radical. In this way each nitroxyl radical can terminate up to ten free radical chains.³

Nitroxyl radicals are also capable of quenching excited aliphatic ketones.²⁵ However, the uniqueness of hindered amines among commercial uv stabilisers appears to hinge on their ability to undergo the preceding reactions and stop or retard the propagation of the free radical chain reactions.

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