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Antioxidant activity of aromatic cyclic amine derivatives

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Abstract

The antioxidant activities of indolines, indoles, and 1,2,3,4-tetrahydroquinolines in the oxidation of tetralin at 61 °C induced by an azo-initiator were evaluated. Indoline itself and indolines with a methyl or methoxy group were strong antioxidants in this tetralin system. Although indoles and 1,2,3,4-tetrahydroquinolines did not have an antioxidant effect, 5-hydroxyindole and 6-methoxy-1,2,3,4-tetrahydroquinolines were potently antioxidant. Among the antioxidants tested, 5-hydroxyindole exhibited the highest induction period, 1.7 times that of BHT. A semiempirical MNDO-AM1 calculation was applied to study hydrogen abstractions of antioxidants in the chain process of autoxidation. These results indicated that the rates of oxidation during the induction period correlated with the dissociation energies of the N–H bond.

Keywords: Antioxidant activity; Indoline; Indole; Tetrahydroquinoline; Bond dissociation energy

1. Introduction

No organic substance is entirely stable under atmospheric conditions. Oils, plastics, rubber products etc, are all degraded by various factors, especially by the action of reactive oxygen-derived species, a process known as autoxidation, with loss of chemical and physical properties. Consequently, the inhibition of oxidation is important in the chemical industry and various antioxidants are now on the market. On the other hand, the stabilization of vinyl monomers during processing, storage and transportation is a great problem, especially in terms of safety, because the polymerization reaction is exothermic. To prevent uncontrolled polymerization, inhibitors such as *tert*-butylcatechol and hydroquinone are used.

The major pathway for the oxidation of organic materials involves a radical chain mechanism. Peroxyl radicals abstract phenolic hydrogen from phenols, and the resulting phenoxyl radical then scavenges a second peroxyl radical to form nonradical products.

Studies on hindered phenols have greatly advanced the use of antioxidants for polymers, especially polyolefines. For example, 2,6-di-*tert*-butyl-4-methylphenol (BHT) and tetrakis(3-(3,5-di-*tert*-butyl-4-hydroxyphenyl) propionate have been commercialized by chemical companies. Also, in rubber technology, amines such as *N*-(1,3-dimethylbutyl)-*N*′-phenyl-*p*-phenylenediamine and *N*-isopropyl-*N*′-pheny-*p*-phenylenediamine are well-known to provide an excellent antioxidant and antiozonant activity against heat, oxygen and ozone.

As polymers and other chemical materials are being used under more severe conditions, it is worth investigating the structure–activity relationships of antioxidants. Previously, we reported that phenothiazines are potent chain-breaking antioxidants for the autoxidation of tetralin [1]. The results indicated that the rates of oxidation during induction period were correlated with the dissociation energy of the N–H bond. In the present study, we compared the antioxidant activities of aromatic cyclic amine derivatives, indolines, indoles and 1,2,3,4-tetrahydroquinolines, in the autoxidation of tetralin. Furthermore, we discuss their antioxidant activities in connection with their dissociation energies for the O–H bond, D(O–H) and the N–H bond, D(N–H) calculated using a semiempirical molecular-orbital method.

2. Results

The antioxidants examined in this study were divided into the three classes shown in Table 1: indolines (**1a–e**), indoles (**2a–d**) and 1,2,3,4-tetrahydroquinolines (**3a–f**).

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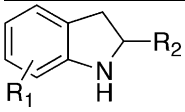
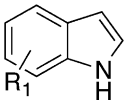
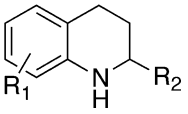
Table 1
Antioxidant activities and dissociation energy of the N–H bond

Structure	Compd no.	R_1	R_2	t_{inh} (min)	R_{inh}/R_0[a]	D(N–H) (kcal/mol)
	**1a**	H	H	319	0.0024	90.0
	1b	5-CH_3	H	236	0.0026	89.7
	1c	7-CH_3	H	300	0.0047	89.4
	1d	5-OCH_3	H	231	0.0009	88.0
	1e	H	CH_3	326	0.0069	91.7
	**2a**	H		5	0.3479	91.7
	2b	5-CH_3		10	0.3253	91.5
	2c	5-OCH_3		3	0.3552	92.1
	2d	5-OH		446	0.0033	92.1 86.2[b]
	**3a**	H	H	34	0.0943	88.2
	3b	6-CH_3	H	65	0.0791	87.7
	3c	8-CH_3	H	39	0.0690	87.9
	3d	6-OCH_3	H	262	0.0392	86.1
	3e	H	CH_3	18	0.1625	89.9
	3f	6-OCH_3	CH_3	195	0.0274	85.7

[a] $R_0 = 1.71\times10^{-5}$ M s^{-1}
[b] Value of D(O–H).

The antioxidant activity of various cyclic amines in the oxidation of tetralin induced by α,α′-azobisisobutyronitrile (AIBN) at 61 °C was assessed. A selected example of the oxidation in the absence and presence of the antioxidants is shown in Fig. 1. The oxidation proceeded smoothly in the absence of an antioxidant (control) without a noticeable induction period (t_{inh}) and a constant rate of oxygen uptake was observed. In the presence of **1a**, **1d** and **3d**, the rate of oxygen uptake was significantly suppressed and a distinct induction period was observed. However, indoles **2a**, **2c** and 1,2,3,4-tetrahydroquinoline **3a** did not suppress the oxidation. As shown in Fig. 1, the rate of oxidation after the induction period was similar to that in the absence of antioxidant.

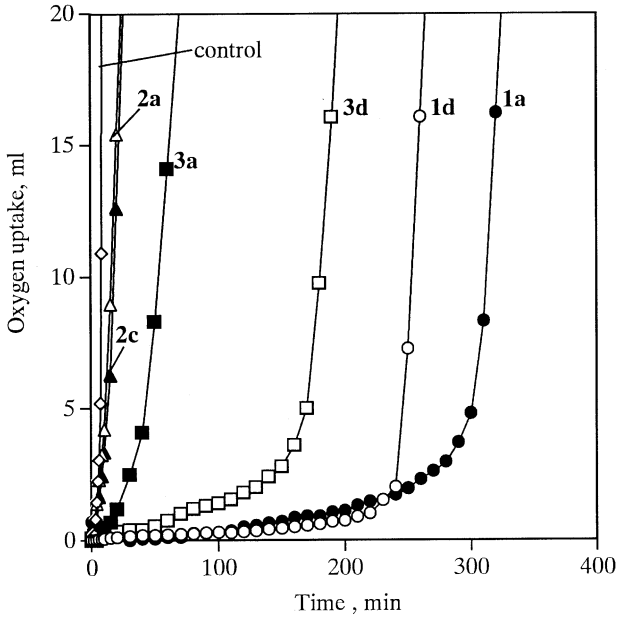


Fig. 1. Rate of oxygen uptake in the oxidation of tetralin initiated by 10.0 mM AIBN in the absence (control) and presence of 1.03 mM antioxidant at 61 °C under oxygen.

3. Discussion

3.1. Antioxidant activity denoted by induction period

The t_{inh} value shows how much does the antioxidant traps the peroxyl radical. The data regarding the antioxidant activity of **1**–**3**, denoted by t_{inh}, are shown in Table 1 and Fig. 2. Indolines **1a** and **1e** with a methyl group at the 2-position showed much higher t_{inh} values, i.e. 319 and 326 min, than BHT ($t_{inh} = 258$ min). However, the t_{inh} values of indolines **1b**–**d** with a methyl or methoxy group at the aromatic ring are all lower than the value for the unsubstituted indoline **1a**. In general, however, the introduction of electron releasing groups such as alkyl substituents to the aromatic ring increases the antioxidant activity, whereas electron attracting groups decrease it. In fact, Mukai et al. [2] reported that the antioxidant activity of tocopherols depends on the number of alkyl substituents at the aromatic ring rather than the position of the substituent. Among these indolines, the t_{inh} values increase in the order **1e**, **1a**, **1c** > **1b**, **1b**. Judging from the t_{inh} value, antioxidant activities of indolines **1e**, **1a** and **1c** are similar or slightly higher than that of BHT.

It is of interest to elucidate whether the conjugated double bond in **2a**–**c** has a remarkable decreasing effect on the antioxidant activity compared to **1**. Indole **2a**, and indoles **2b** and **2c** with a methyl and methoxy group

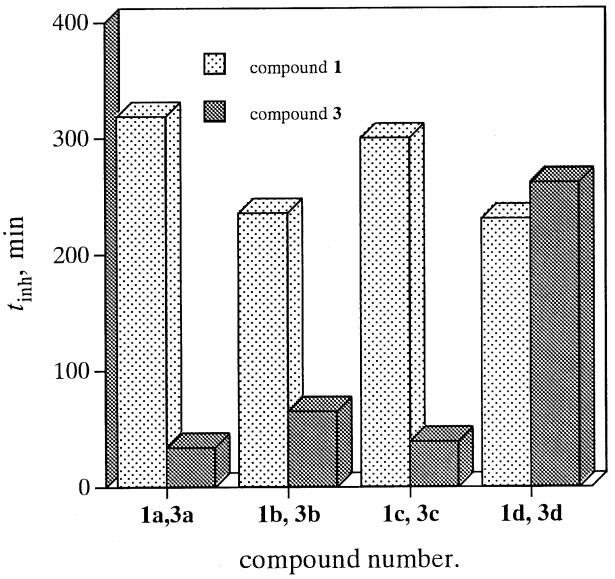


Fig. 2. Antioxidant activity denoted by t_{inh} of **1** and **3**.

at the 5-position, respectively, did not act as antioxidants. However, 5-hydroxyindole **2d** showed a marked increase in the t_{inh} value. The 5-hydroxyindole exhibits the t_{inh} value 1.7 times that of BHT. This shows that the strong effect of hydroxyindole **2d** on radical scavenging is based upon the presence of the OH group.

Efficient phenolic antioxidants are known to terminate the peroxidation of free radical chains by donating a phenolic hydrogen atom, reaction 1. A high rate for reaction 1 is expected to correlate with a low O–H bond dissociation energy.

$$\mathrm{ROO}\cdot + \mathrm{ArOH} \rightarrow \mathrm{ROOH} + \mathrm{ArO}. \quad (1)$$

Considerable effort has therefore been devoted to the measurement of D(O–H) for phenols. For example, Ingold et al. [3] reported that a substituent affects the bond dissociation energy of antioxidants. Therefore, we calculated the D(N–H) and D(O–H) for **2d** with a semiempirical AM1 [4] molecular orbital calculation using the program MOPAC 94. The bond dissociation energies of N–H (D(N–H)) and O–H (D(O–H)) are listed in Table 1. The dissociation energy of the O–H bond was calculated to be 5.9 kcal mol^{-1} weaker than that of the N–H bond. The values of the antioxidant activity and the dissociation energy suggest that the initial step in the inhibition of oxidation must be the donation of a phenolic hydrogen atom at the 5-position by the peroxyl radical.

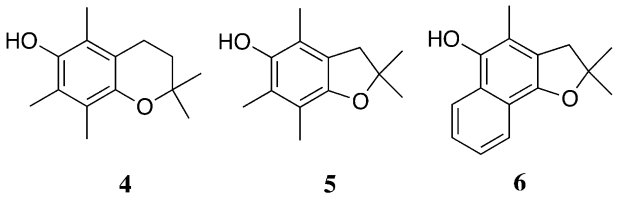
The 1,2,3,4-tetrahydroquinoline **3a** itself and those having a methyl group at the 2-, 6- and 8-position did not suppress the oxidation. On the other hand, 6-methoxy-1,2,3,4-tetrahydroquinoline **3d** suppressed the oxidation, but the introduction of a methyl group at the 6-position resulted in a reduction in antioxidant activity.

3.2. Antioxidant activity as measured by R_{inh}/R_0

Niki et al. [5] reported that the efficiency of antioxidants can be estimated from R_{inh}/R_0, where R_{inh} is the rate of oxidation during the induction period inhibited by antioxidant and R_0 is the rate of oxidation in the absence of antioxidant. In other words, the value R_{inh}/R_0 shows how much the antioxidant reduces the rate of oxidation compared with control. Therefore, we used R_{inh}/R_0 value instead of R_{inh} as a guide to the antioxidant activity. In order to estimate the efficiency of R_{inh}/R_0, we first measured the oxidation of tetralin in the presence of BHT induced by AIBN under the same reaction conditions as those used in Fig. 1. BHT had a R_{inh}/R_0 value of 0.0169. The rate constant k_{inh} of BHT for the oxidation of styrene at 30 °C induced by AIBN was reported to be $k_{inh} = 1.4\times10^4$ M^{-1} s^{-1} [6].

The antioxidant activity as measured by R_{inh}/R_0 for **1**–**3** is listed in Table 1. The results indicate that indoline **1a** itself was a potent antioxidant. Those indolines with a methyl group on the benzene ring or heterocyclic ring have reactivity similar to or slightly less than that of the parent indoline **1a**. The R_{inh}/R_0 value of **1d** is much smaller than the other indolines. This indicates that the reaction of indoline **1d** with peroxyl radicals is enhanced by the 5-methoxy group. Indole **2a** did not act as an antioxidant and the introduction of an electron-donating group at the 5-position also did no suppress the oxidation. However, the 5-hydroxyindole **2d** was a good antioxidant. 1,2,3,4-Tetrahydroquinoline **3a** itself was a poor antioxidant. On the other hand, tetrahydroquinoline with a methoxy group at the 6-position acted as good antioxidants but those with a methyl group at the 2-position did not suppress the oxidation.

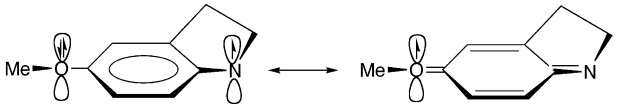
Gilbert [7] reported that dihydrofuran **5** quenches peroxyl radicals 1.5 times more rapidly than does chroman **4** (Scheme 1). This difference is ascribed to the value of the dihedral angle. The dihedral angle is 17° for **4** but less than 17° for **5**. Barclay reported also that the k_{inh} value of dihydronaphtofuran **6** was 10 times larger than that for α-tocopherol [8,9]. The higher antioxidant activity was attributed to additional delocalization of the phenoxyl radical into the fused aromatic ring. Moreover, Burton and Ingold reported that 4-methoxyphenols was ~5 times as potent as that of 4-methylphenols [10]. The superior antioxidant properties of the 4-methoxyphenol result from the stabilization of the



4 **5** **6**

Scheme 1.

phenoxyl radical, due to improved resonance overlap between the phenoxyl radical and the ether oxygen of the methoxy group. The stabilization depends on the dihedral angle between the direction of the 2p orbital of the methoxy oxygen and a line perpendicular to the aromatic plane. It is therefore of interest to compare the antioxidant activity of **3** having a 6-membered ring and **1**. The 1,2,3,4-tetrahydroquinolines **3** had higher R_{inh}/R_0 values than did the indolines derivatives with a 5-membered ring. From comparisons between **1a** and **3a**, **1b** and **3b**, **1c** and **3c**, **1d** and **3d**, **1e** and **3e**, the R_{inh}/R_0 values are about 15–40 times higher for **3** than for **1**. In view of the above structure–activity relationships, we assume that the main factor causing the rise in antioxidant activity of **1** compared with **3** is stereoelectronic effects stabilizing the indolinyl radical formed when indoline scavenges the peroxyl radical; the indolinyl radical would be expected to further delocalize with the aromatic π electron system. In fact, among the antioxidants **1a**–**e**, 5-methoxyindoline **1d** was found to have a lowest R_{inh}/R_0 value. This enhancement of R_{inh}/R_0 by a 5-methoxy group is due to stabilization of the indolinyl radical by delocalization of the unpaired electron to the p-type lone pair of the methoxy oxygen (Scheme 2). [10]



Scheme 2.

3.3. Relationship between N–H bond dissociation energy and R_{inh}/R_0

Previously, we reported on the hydrogen abstraction of antioxidants in the chain process of antioxidation. The experimental results showed that electrochemical oxidation potential [11] and bond dissociation energy [12] were associated with antioxidant activity.

On this basis, the R_{inh}/R_0 value is plotted against the estimated N–H bond dissociation energy. The D(N–H) values of antioxidants tested were affected by the structure. Our calculations indicate that a methoxy group at the 5-position for **1** and 6-position for **3** has the effect of markedly weakening the N–H bond. A methyl substituent at the 6-position, by contrast, produces an increase in D(N–H). That is, based on the D(N–H) values, indolines and 1,2,3,4-tetrahydroquinolines ranked in the order **1e** > **1a**,**1b**,**1c** > **1d** and **3e** > **3a**,**3c**, **3b** > **3d** > **3f**, respectively. On the other hand, the R_{inh}/R_0 values decreased in a roughly similar order to the D(N–H) values: **1e** > **1c** > **1b**,**1a** > **1d**, and **3e** > **3a**,**3b** > **3c** > **3d** > **3f**. These results suggest that the antioxidant activities of **1** and **3** are correlated with the ease of abstraction of a hydrogen atom from the N–H bond. Therefore, we examined the relationships between the antioxidant activity and the values of D(N–H). In Fig. 3, the calculated D(N–H) values for compounds **1** and **3** are plotted against the R_{inh}/R_0 value for the oxidation of tetralin initiated by AIBN at 61 °C. As shown in this figure, the plotted points roughly fall on individual lines for the indolines **1** and 1,2,3,4-tetrahydroquinolines **3**. In each case, however, the R_{inh}/R_0 values decreases with decreasing D(N–H). From these results, the antioxidant activity is dependent not only on the strength of the resonance effect [5] but also on the dissociation energy of the N–H bond.

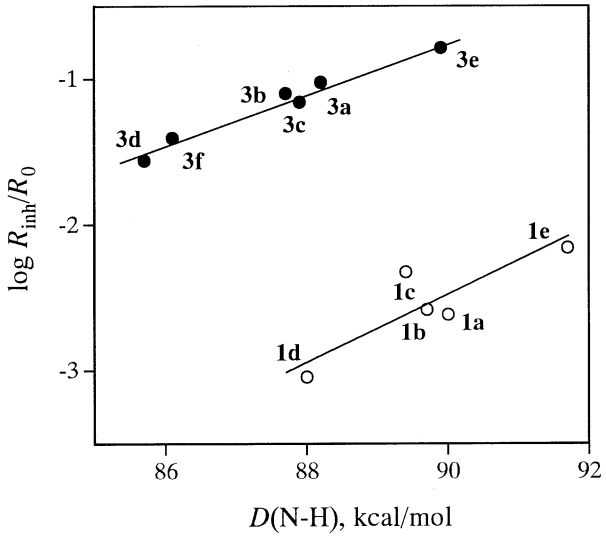


Fig. 3. Plot of bond dissociation energy (D(N–H)) vs. R_{inh}/R_0 for **1** and **3**.

4. Experimental

4.1. General

Nuclear magnetic resonance spectra were recorded with a Jeol GSX-400 spectrometer operated at 400 MHz for ^{1}H and at 100.6 MHz for ^{13}C in $CDCl_3$, and chemical shift data are with reference to $(CH_3)_4Si$. Mass spectra were measured with a Perkin-Elmer model 910 spectrometer operating in the electron impact mode (70 eV).

4.2. Assay for antioxidant activity

The rate of oxygen absorption was measured as a function of time under 760 Torr (1 Torr = 133.3 Pa) of O_2 with 50.0 ml of tetralin containing an antioxidant (1.03 mM) and α,α′-azobisisobutyronitrile (AIBN) (10.0 mM) as the initiator. The oxidation temperature was maintained at 61 ± 0.1 °C. The t_{inh} value was graphically

determined from the length of time between initiator injection and the point of intersection of the tangents to the oxidation curve corresponding to the initial inhibited and final uninhibited rates of oxidation.

4.3. Molecular orbital calculations

The geometries were optimized to give the heat of formation at the singlet ground state using the restricted Hartree–Fock method for antioxidants, and at the doublet using the unrestricted Hartree–Fock method for radicals. The D(N–H) value was obtained from the enthalpy of the optimum structures of antioxidants and relative radicals, as follows:

$$D(\mathrm{N-H}) \text{ or } D(\mathrm{O-H}) \text{ (kcal mol}^{-1}) = E_r + E_H - E_o$$

where E_r is enthalpy of radical, E_H is enthalpy of hydrogen radical, E_o is enthalpy of antioxidant.

4.4. Materials

Indolines **1a** and **1e**, indoles **2a**, **2b**, **2c** and **2d**, 1,2,3,4-tetrahydroquinoline **3a** were obtained from Aldrich. Indolines **1b–d** were prepared by reducing the corresponding indoles with $Na[B(CN)H_3]$. In a typical preparation, indole **2b** (0.08 g, 0.61 mmol) was dissolved in acetic acid (4.8 ml) and $Na[B(CN)H_3]$ (0.21 g, 3.3 mmol) was added in portions with stirring at room temperature. The resulting mixture was stirred for 15 min and then poured into 25% aqueous sodium hydroxide. Organic materials were extracted with ether and extract was dried over magnesium sulfate. The ether layer was concentrated in vacuo to give almost pure **1b**. 1,2,3,4-Tetrahydroquinolines **3b**, **3c**, **3d**, **3e**, [13] and **3f** were prepared by reducing the corresponding quinolines with $NaBH_4$–$NiCl_2$ system [13].

4.4.1. 5-Methylindoline (**1b**)

Pale yellow oil. Yield, 98%. ^{1}H NMR: $\delta = 2.23$ (*s*, 3H), 3.01 (*t*, $J = 8.3$Hz, 2H), 3.56 (*t*, $J = 8.3$Hz, 2H), 4.34 (*s*, 1H), 6.65 (*d*, $J = 7.8$Hz, 1H), 6.86 (*d*, $J = 7.8$Hz, 1H), 6.97 (*s*, 1H). ^{13}C NMR: $\delta = 20.8$, 29.8, 47.3, 110.9, 125.6, 127.8, 130.1, 130.5, 146.6. MS *m*/*z* (rel. intensity):134(9), 133 (M^+, 86), 132 (100), 131 (10), 130 (12), 116 (14), 117 (32), 77 (11).

4.4.2. 7-Methylindoline (**1c**)

Yield, 98%. ^{1}H NMR: $\delta = 2.12$ (*s*, 3H), 3.03 (*t*, $J =$ 8.3Hz, 2H), 3.53 (*t*, $J = 8.3$Hz, 1H), 6.63 (*t*, $J = 7.3$Hz, 2H), 6.84 (*t*, $J = 7.3$Hz, 1H), 6.97 (*d*, $J = 7.3$Hz, 1H). ^{13}C NMR: $\delta = 16.7$, 30.0, 46.9, 118.5, 118.6, 121.8, 127.9, 128.4, 149.7. MS *m*/*z* (rel. intensity): 134 (11), 133 (M^+, 99), 132 (100), 131 (11), 130 (12), 118 (18), 117 (39), 77 (11).

4.4.3. 5-Methoxyindoline (**1d**)

Yield, 98%. ^{1}H NMR: $\delta = 2.98$ (*t*, $J = 8.4$Hz, 2H), 3.47 (*t*, $J = 8.4$Hz, 2H), 3.60 (*s*, 1H), 3.72 (*s*, 3H), 6.55–6.61 (*m*, 2H), 6.61–7.23 (*m*, 1H). ^{13}C NMR: $\delta = 30.4$, 47.8, 55.9, 110.1, 111.5, 112.1, 131.1, 145.3, 153.5. MS *m*/*z* (rel. intensity): 150(10), 149 (M^+, 81), 148 (9), 135 (12), 134 (100), 133 (14), 106 (9).

4.4.4. 6-Methyl-1,2,3,4-tetrahydroquinoline (**3b**)

Yield, 94%, pale yelow oil. ^{1}H NMR: $\delta = 1.88$–1.94 (*m*, 2H), 2.19 (*s*, 3H), 2.73 (*t*, $J = 6.3$Hz, 2H), 3.26 (*t*, $J = 6.3$Hz, 2H), 6.39–6.50 (*m*, 1H), 6.70–6.81 (m, 2H). ^{13}C NMR: $\delta = 20.4$, 22.5, 26.9, 114.3, 121.2, 126.1, 127.2, 129.9, 142.2. MS *m*/*z* (rel. intensity):147 (11), 146 (M+,100), 145 (89), 132 (24), 131(18), 130 (17), 117 (14), 91 (11).

4.4.5. 8-Methyl-1,2,3,4-tetrahydroquinoline (**3c**)

Yield, 99%, pale yellow oil. ^{1}H NMR: $\delta = 1.88$–1.94 (*m*, 2H), 2.05 (*s*, 3H), 2.76 (*t*, $J = 6.3$Hz, 2H), 3.34 (*t*, $J = 6.3$Hz, 2H), 3.57 (*s*, 1H), 6.51–6.55 (*m*, 1H), 6.82–6.86 (*m*, 2H). ^{13}C NMR: $\delta = 17.1$, 22.1, 27.3, 42.3, 116.2, 120.7, 120.9, 127.2, 127.7, 142.5. MS *m*/*z* (rel. intensity): 148 (11), 147 (M^+, 100), 146 (77), 132 (29), 131 (20), 130 (15), 117 (12).

4.4.6. 6-Methoxy-1,2,3,4-tetrahydroquinoline (**3d**)

Yield, 99%, pale yellow oil. ^{1}H NMR: $\delta = 1.90$–1.94 (*m*, 2H), 2.75 (*t*, $J = 6.3$Hz, 2H), 3.25 (*t*, $J = 6.3$Hz, 2H), 3.72 (*s*, 3H), 6.43–6.45 (*m*, 1H), 6.56–6.59 (*m*, 2H). ^{13}C NMR: $\delta = 22.5$, 27.2, 42.3, 112.7, 114.7, 115.6, 122.8, 138.7, 151.6. MS *m*/*z* (rel. intensity): 163 (M+, 63), 149 (10), 148 (100).

4.4.7. 2-Methyl-6-methoxy-1,2,3,4-tetrahydroquinoline (**3f**)

Yield 95% pale yellow oil. ^{1}H NMR: $\delta = 1.17$ (*d*, $J = 6.4$Hz, 3H), 1.55–1.61 (*m*, 1H), 1.86–1.92 (*m*, 1H), 2.67–2.70 (*m*, 1H), 2.78–2.82 (*m*, 1H), 3.29–3.32 (*m*, 1H), 3.39 (*s*, 1H), 3.70 (*s*, 3H), 6.41–6.43 (*m*, 1H), 6.56–6.58 (*m*, 2H). ^{13}C NMR: $\delta = 22.5$, 26.9, 30.3, 47.3, 47.5, 112.6, 112.8, 114.6, 115.0, 122.3, 138.8,151.6. MS *m*/*z* (rel. intensity): 177 (M^+, 62), 163 (8), 162 (100), 147 (10).

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