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*The phenol trimer, 5,5′,5″-trichloro-1,1′:3′,1″-terphenyl-2,2′,2″-triol (***1***), facilely affords the 1:1 complex (***1***) with triethylamine owing to its enhanced acidity. IR spectra reveal that* **I** *is a proton transfer complex. In the X-ray structure of* **I**, *a long phenoxide C−O bond is observed that may be due to unusual* sp^3 *hybridization of the phenoxide oxygen atom caused by strong intra- and inter-molecular hydrogen bonding.*

Keywords: amine complex; bond length; phenoxide; proton transfer complex; X-ray structure

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INTRODUCTION

For the purpose of crystal engineering [1], the simple hydrogen bond such as OH/O or OH/N is of limited use because the C−O(H) bond may rotate so that the geometry cannot be predicted, and its interaction energy (*ca*. 5 kcal mol^{-1}) is not particularly strong for becoming the principal force in regulating the crystal structure [2]. Concerning the latter issue, the proton transfer complex should be a more promising candidate, the interaction energy of which, *ca*. 10 kcal mol^{-1} or more, is considerably larger. A proton transfer complex can be made up of a combination of acid and base. Although phenol can act as an acidic component, a combination of phenol and amine scarcely affords a proton transfer complex because of the weak acidity of phenols. In the present paper, we have focused our attention on the phenol trimer (5,5′,5″-trichloro-1,1′:3′,1″-terphenyl-2,2′,2″-triol, **1**) [3], the acidity of which is expected to be enhanced by intramolecular hydrogen bonding stabilizing its conjugate base (**1a**) as observed in bis(2-hydroxyphenyl)methane [4], so that a proton transfer complex with amines will be given.

RESULTS AND DISCUSSION

The 1:1 triethylamine complex (**I**) was prepared by recrystallization of **1** in the presence of triethylamine (Et_3N) in dichloromethane. The stoichiometric ratio of **I** was determined by ^1H NMR spectroscopy to be 1:1. IR spectra reveal that **I** is a proton transfer complex as expected. Broad absorption attributed to the stretching vibration of O−H bond is observed around 2300 cm^{-1} in **I** (Fig. 1(a)), while at 3400−3200 cm^{-1} in **1** (Fig. 1(b)), indicating that the O−H and N−H groups are hydrogen-bonded to a phenoxide oxygen. Thus, **I** should be represented as (**1a**)(Et_3NH^+) rather than (**1**)(Et_3N). It is deducible that it is the central phenolic moiety that releases the proton to become the phenoxide to which Et_3NH^+ is hydrogen-bonded (see Scheme). Otherwise, a hydroxy group hydrogen-bonded to a *neutral* OH group would be observed around 3400−3000 cm^{-1}.

The structure of **I** mentioned above is substantiated by X-ray analysis (Fig. 2). Compound **1a** adopts pseudo-*Cs* symmetry, and both hydroxy groups on the terminal phenol moieties and the NH group are hydrogen-bonded to the central oxygen atom. It is noteworthy that the C22−O2 bond length (1.346(2) Å) is as long as C12−O1 and C32−O3 ((1.358(2) and 1.363(2) Å, respectively), being comparable to the mean value of the neutral phenolic C−O bond length (1.363 Å) [5]. It is generally known that, in phenoxide anions, the oxygen is

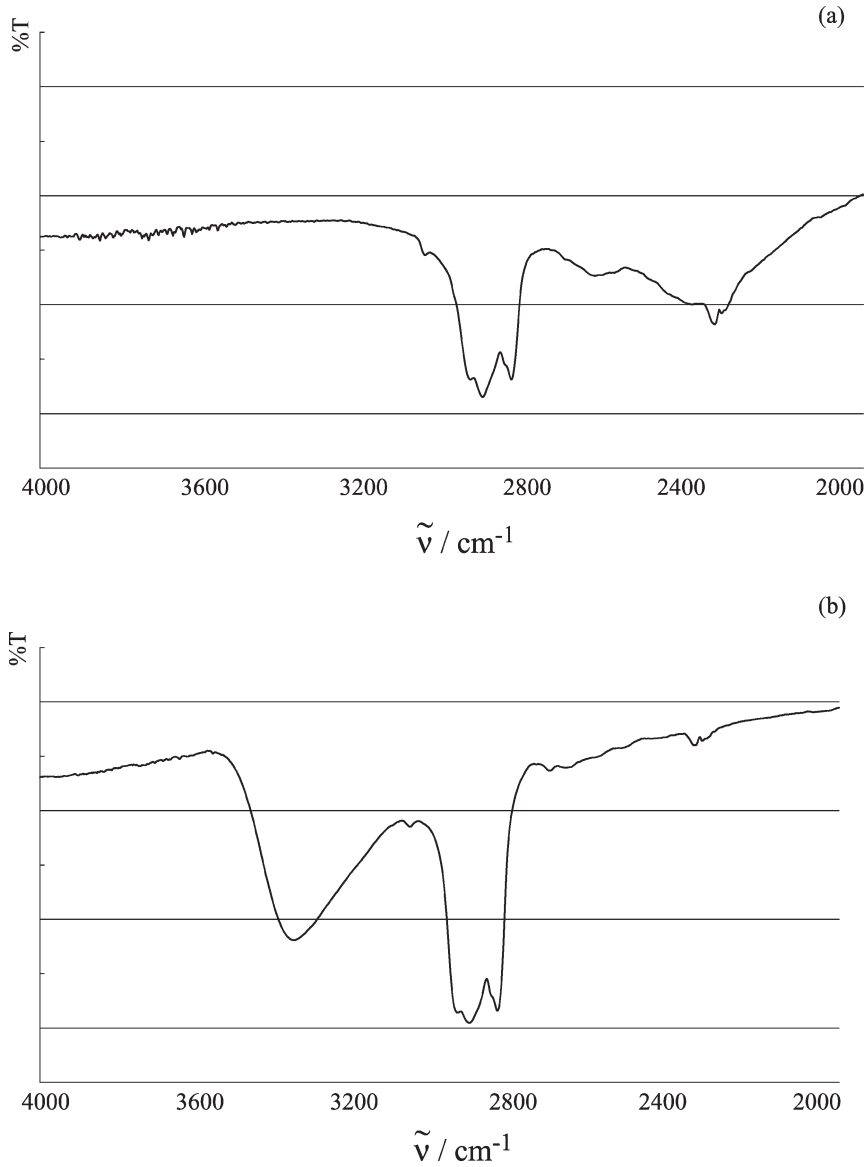


FIGURE 1 IR spectra of **I** (a) and **1** (b).

sp^2 hybridized so that the negative charge is delocalized onto benzene ring (by which mechanism phenolic hydroxy groups are more acidic than alcoholic ones), and consequently the phenoxide C−O bond has

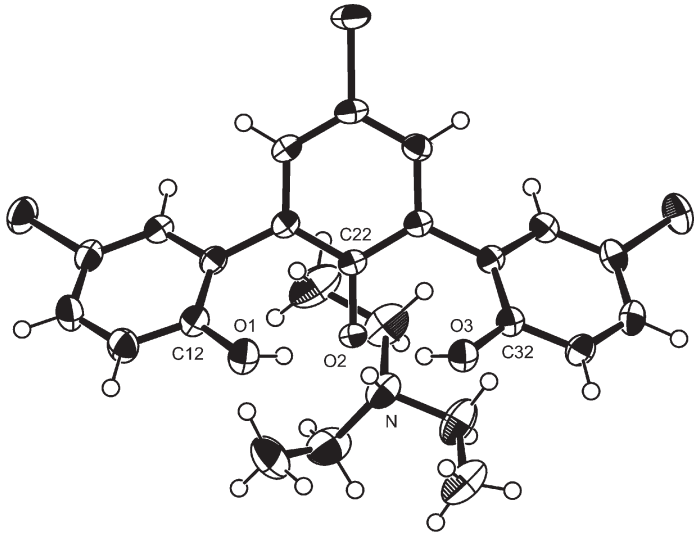
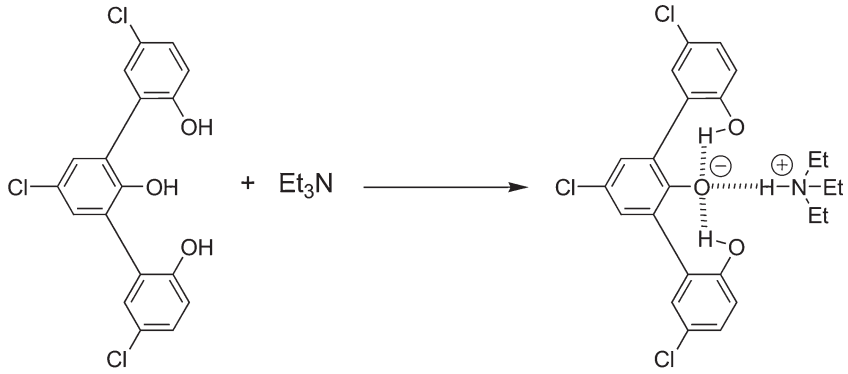


FIGURE 2 X-ray structure of **I**. Hydrogen atoms were found in a differential Fourier map.

partially double-bond character and is shorter than a neutral phenolic C–O bond. Theoretical study predicts the interatomic distance of phenoxide C–O to be 1.27 Å for $C_6H_5O^-$ (B3LYP) [6]. Nevertheless, it appears that O2 in **I** adopts sp^3 hybridization. Although sp^3 hybridization is less favorable by the loss of resonance energy, this may be compensated forby strong hydrogen bonding to O2 on which negative



1 **I**

SCHEME 1

charge is localized. Moreover, four atoms around O2 locate at nearly ideal positions for sp^3 hybridized O2: C22, O1, O3, and N are arranged in a tetrahedral manner, where the C22−O2···O1, C22−O2···O3, and C22−O2···N angles are 98°, 98°, and 113°, respectively. In such an atomic arrangement, orbital interaction should be stronger when O2 adopts sp^3 hybridization rather than sp^3 hybridization. Namely, in **I**, proton transfer complexation gives rise to not only strong connection between **1a** and Et_3NH^+ but also regulation of their geometry.

In conclusion, the X-ray structure and IR spectra of the proton transfer complex **I** consisting of phenol trimer (**1**) and triethylamine, are reported. An unusually long phenoxide bond (C22−O2) and a tetrahedral arrangement of hydrogen bonded groups around O2 are observed, which are attributable to sp^3 hybridization of O2.

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