ISSN 1070-3632, Russian Journal of General Chemistry, 2006, Vol. 76, No. 6, pp. 989–991. © Pleiades Publishing, Inc., 2006.
Original Russian Text © A.V. Chernova, R.R. Shagidullin, S.V. Bukharov, G.N. Nugumanova, N.A. Mukmeneva, 2006, published in Zhurnal Obshchei Khimii, 2006, Vol. 76, No. 6, pp. 1034–1036.

Molecular Structure of 2,4,6-Tris(di-*tert*-butyl-4-hydroxybenzyl)resorcinol in the Crystal and in Solution, According to IR Data

A. V. Chernova[a], **R. R. Shagidullin**[a], **S. V. Bukharov**[b],
G. N. Nugumanova[b], **N. A. Mukmeneva**[b]

[a] *Arbuzov Institute of Organic and Physical Chemistry,*
Kazan Research Center, Russian Academy of Sciences,
ul. Arbuzova 8, Kazan, Tatarstan, 420088 Russia
[b] *Kazan State Technological University, Kazan, Tatarstan, Russia*

Received July 7, 2005

Abstract— 2,4,6-Tris(3,5-di-*tert*-butyl-4-hydroxybenzyl)resorcinol in the crystal and in solution has a similar steric structure, favorable for its performance as peroxyl radical scavenger.

DOI: 10.1134/S1070363206060247

The antioxidative performance of polymer stabilizers is largely determined by their structure. Therefore, elucidation of the steric structure of polyphenolic stabilizers is an urgent problem.

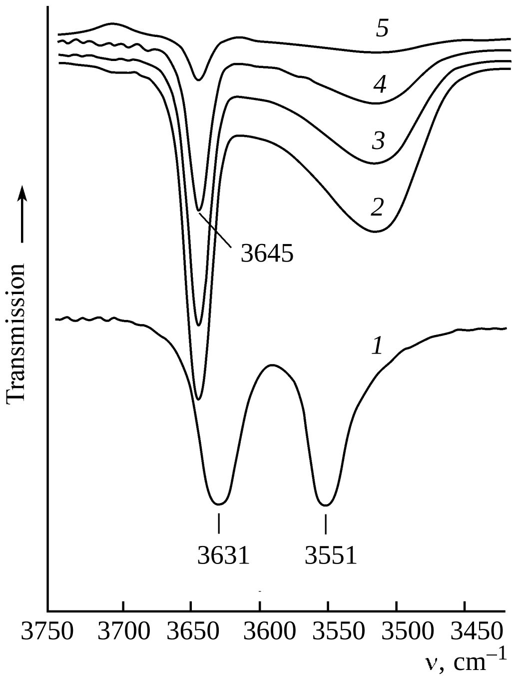
2,4,6-Tris(3,5-di-*tert*-butyl-4-hydroxybenzyl)resorcinol (**I**) is an effective stabilizer for many polymers [1, 2]. The previously performed single crystal X-ray diffraction study showed that the molecule of **I** has a “basket” structure with the resorcinol ring plane as a “bottom” and 3,5-di-*tert*-butyl-4-hydroxybenzyl fragments as “walls” [3]. Similar steric arrangement of sterically hindered hydroxybenzyl fragments is also observed in the molecule of 1,3,5-tris(3,5-di-*tert*-butyl-4-hydroxybenzyl)-2,4,6-trimethylbenzene [4]. It is believed that such a structure ensures high antioxidative activity of this stabilizers, because the “basket” edges act as a trap for capture and deactivation of peroxy radicals [5].

In addition to X-ray diffraction data, it seems urgent to examine compound **I** by IR spectroscopy and elucidate the relationships of the IR characteristics of **I** with the structure and properties of the molecules not only in the crystal phase, but also in solutions, since the solutions are more interesting from the practical viewpoint.

The IR spectrum of a crystalline sample of **I** is consistent with its structure and contains the following characteristic absorption bands, cm^{-1}: 3631/3551 (ν_{OH}); 2954, 2924, 2872, 1395, 1363 (CH_3, CH_2); 3071, 3005, 1609, 1480 (Ar); 1350–1000 (>C–O, >C–C, δ_{Ar}) [6].

Of most interest for us is the region of ν_{OH}. The pattern observed in the IR spectra of KBr pellets and CCl_4 solutions of **I** is qualitatively similar. As in the spectrum of the crystal, the spectrum of the solution contains a narrow peak at 3645 cm^{-1} and a broadened band with a maximum at 3517 cm^{-1} (see figure). As for the nature of these absorption bands, the wavenumber of the high-frequency component, 3645 cm^{-1}, virtually coincides with the value given in the literature for ν_{OH}(free) of sterically hindered cis-hydroxyl in the *o*-*tert*-butylphenol molecule [7]. From the intensity of this band, it is possible to estimate the number of free OH groups in the molecule of **I**. For this purpose, the molar extinction coefficient in the maximum of the band at 3645 cm^{-1} in the spectrum of a solution of I, 750 mol^{-1} cm^{-1} l, was compared to that of the band at 3640 cm^{-1} of (3,5-di-*tert*-butyl-4-hydroxybenzyl)thiourea [8] chosen as reference (one free OH group in similar environment), 280 mol^{-1} cm^{-1} l. The ratio of 750 to 280 is 2.7, i.e., the intensity of the band at 3645 cm^{-1} corresponds to three free OH groups in the hydroxybenzyl fragments of **I**. Certain differences between the frequencies in solution (3645 cm^{-1}) and in the crystal phase (3631 cm^{-1}) are quite natural and are due to the effect of the medium.

The low-frequency band at 3517 (in CCl_4) or 3551 cm^{-1} (in KBr) should be assigned to resorcinol hydroxyls of the “basket bottom.” As the solutions are diluted from 10^{-4} to 10^{-5} M, the positions of the maxima and the ratio of the peak intensities of the bands at 3645 and 3517 cm^{-1} remain essentially unchanged, suggesting that the hydroxy groups in **I** are



Fragments of the IR spectra of **I** in (*1*) KBr and (*2*–*5*) CCl_4. $c_{\mathbf{I}}$, M: (*2*) 9.0×10^{-4}, (*3*) 2.4×10^{-4}, (*4*) 1.3×10^{-4}, and (*5*) 3.1×10^{-5}. Cell thickness, cm: (*2, 3*) 2 and (*4, 5*) 4.

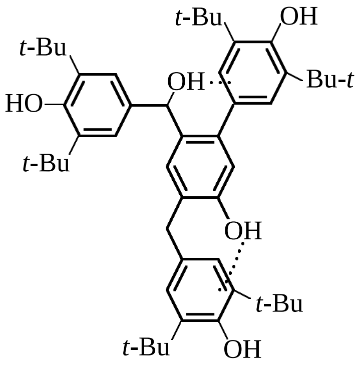
not involved in the self-association. The significant low-frequency shift of the resorcinol hydroxyl frequencies in the spectra of **I** (64 cm^{-1} for the crystal and 98 cm^{-1} for solutions) relative to ν_{OH}(free) of 2-methylresorcinol [9] should be attributed to an intramolecular hydrogen bond. The asymmetry of this band suggests certain structural nonequivalence of two resorcinol hydroxyls, which is consistent with the X-ray diffraction data [3] on the distortion of the molecular symmetry in the crystal.

The IR data allow us to estimate the contribution of hydrogen bonds to the energy of **I**. We estimated the hydrogen bond energy by the Iogansen intensity rule [9]:

$$-\Delta H = 12.12\Delta A^{1/2},$$

where ΔH is the hydrogen bond energy, and $\Delta A^{1/2} = A^{1/2} - A_0^{1/2}$ is the difference between the square roots of the integral molar intensities (10^4 cm mmol^{-1}) of the absorption bands ν_{OH} of the hydrogen-bonded (A) and free (A_0) OH groups.

By measuring the area S of the peak at 3517 cm^{-1} (in the optical density scale), we obtained A for the solution of **I** in CCl_4: 1.14, or 0.57 per OH group. As A_0 of ν_{OH}(free) we took the value of 0.4 given in [10] for the band at 3615 cm^{-1} of a solution of 3,5-dimethylphenol in CCl_4. This value well agrees with the value we obtained for the band at 3615 cm^{-1} of 2-methylresorcinol in CCl_4 (per OH group): A_0 0.37. Thus, the energy of the intramolecular hydrogen bond in **I** is 1.48 kJ mol^{-1} per OH group, or 2.96 kJ mol^{-1} for two resorcinol hydroxyls in **I**. The value of 1.48 kJ mol^{-1} is close to the energy of the OH···π intramolecular hydrogen bond in 2-benzylphenol (1.38 kJ mol^{-1} [7]), which suggests that the H bond in **I** is of similar type. This assumption is confirmed by the presence of short contacts between the resorcinol hydroxyl protons and carbon atoms of the aromatic rings of the hydroxybenzyl fragments in the crystal of **I** [3].



I

The preservation of the intramolecular OH···π bonds in the solution of **I** suggests that the conformation realized in the liquid phase is largely similar to that in the crystal (“basket”), with somewhat higher mobility of the fragments (as follows from the shift and broadening of the low-frequency ν_{OH} band).

Our results show that the IR spectra of compounds of type **I** allow estimation of the structure and properties of molecules of these compounds in different media. The structure of **I** is favorable for its antioxidative performance in stabilization of both solid polymers and liquid organic media.

EXPERIMENTAL

The IR spectra were recorded on a Bruker Vector-22 Fourier IR spectrometer in the range 4000–400 cm^{-1} with 1 cm^{-1} resolution. Samples were prepared as KBr pellets and CCl_4 solutions. Solution concentration 9×10^{-4}–3×10^{-5} M, cell thickness 2 and 4 cm.

2,4,6-Tris(3,5-di-*tert*-butyl-4-hydroxybenzyl)resorcinol was prepared by the procedure described in [1].

REFERENCES

1. US Patent 4 173 541, 1979, *Ref. Zh. Khim.*, 1980, 9P356P.
2. Bukharov, S.V., Teregulova, E.A., Nugumanova, G.N., Mukmeneva, N.A., Miryasova, F.K., Burilov, A.R., Pudovik, M.A., Nikolaeva, I.L., Kasymova, E.M., and Konovalov, A.I., *Zh. Prikl. Khim.*, 2003, vol. 76, no. 11, p. 1918.
3. Bukharov, S.V., Litvinov, I.A., Gubaidullin, A.T., Nugumanova, G.N., and Mukmeneva, N.A., *Russ. J. Gen. Chem.*, 2002, vol. 72, no. 2, p. 268.
4. Chetkina, L.A., Zavodnik, V.E., and Andrianov, V.I., *Dokl. Akad. Nauk SSSR*, 1978, vol. 242, no. 1, p. 103.
5. Gurvich, Ya.A., Arzamanova, I.G., and Zaikov, G.E., *Khim. Fiz.*, 1996, vol. 15, no. 1, p. 23.
6. Colthup, N.B., Daly, L.H., and Wiberley, S.E., *Introduction to Infrared and Raman Spectroscopy*, New York: Academic, 1964.
7. Bellamy, L.J., *Advances in Infrared Group Frequencies*, London: Methuen, 1968.
8. Bukharov, S.V., Litvinov, I.A., Gubaidullin, A.T., Chernova, A.V., Shagidullin, R.R., Nugumanova, G.N., and Mukmeneva, N.A., *Russ. J. Gen. Chem.*, 2004, vol. 74, no. 11, p. 1734.
9. Iogansen, A.V., *Spectrochim. Acta, Part A*, 1999, vol. 55, nos. 7–8, p. 1585.
10. Lutz, B.T.G., Astarloa, G., Maas, I.H., Janssen, R.G., Verboom, W., and Reinhoudt, D.N., *Vibrat. Spectrosc.*, 1995, vol. 10, no. 1, p. 29.