ISSN 1070-3632, Russian Journal of General Chemistry, 2012, Vol. 82, No. 3, pp. 436–439. © Pleiades Publishing, Ltd., 2012.
Original Russian Text © S.G. Semenov, M.V. Makarova, 2012, published in Zhurnal Obshchei Khimii, 2012, Vol. 82, No. 3, pp. 443–446.

Quantum-Chemical Calculation of Electrooptical Properties of Vanillin Tautomers

S. G. Semenov and M. V. Makarova

St. Petersburg State University, Universitetskii pr., 26, St. Petersburg, 198504 Russia
e-mail: mcmury@yandex.ru

Received April 27, 2011

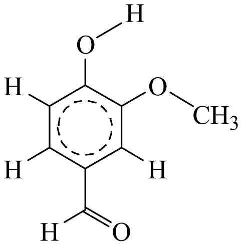
Abstract—Static dipole polarizabilities and hyperpolarizabilities of benzoid and *p*-quinoid molecular forms of vanillin were calculated using quantum-chemical method B3LYP/cc-pVTZ. The dominant benzoid tautomers much exceed in hyperpolarizability the *m*-nitroaniline molecule. Tautomeric transformations and conformational changes significantly affect the vanillin hyperpolarizability. Quinoid tautomers generated by the topochemical reaction of proton transfer between neighboring molecules in a vanillin crystal can promote the second harmonic generation of infrared laser light only as an element of supramolecular nanostructures (linear defects) with a high hyperpolarizability.

DOI: 10.1134/S1070363212030127

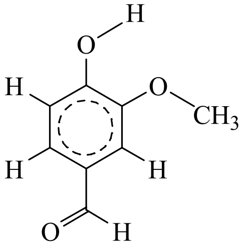
The investigation of single crystals of vanillin (3-methoxy-4-hydroxybenzaldehyde) showed a high conversion efficiency of the laser radiation at a wavelength of 1060 nm (energy of infrared quant 27 kcal mol^{-1}) into the visible light with a wavelength of 530 nm [1]. By its efficiency of the second harmonic generation, vanillin exceeds *m*-nitroaniline, which is commonly used as a model for evaluating the materials with nonlinear optical properties [1–3].

The high vanillin hyperpolarizability is due to the combination in its molecule of electron-donor phenol fragment and electron-acceptor formyl group. In a crystal, the vanillin molecules form a chains with intermolecular hydrogen bonds O–H$_{ac}$···O, and the crystal symmetry [4] is low enough to prevent the manifestation of nonlinear optical properties due to the first hyperpolarizability inherent in these molecules [1, 2].

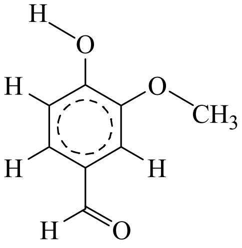
It was found in [5] by quantum-chemical method B3LYP/cc-pVTZ that along with the low-energy benzoid forms of vanillin (*Z*)-B1, (*E*)-B1, (*Z*)-B2, and (*E*)-B2, it may exist in *p*-quinoid forms (*Z*)-Q1, (*E*)-Q1, (*Z*)-Q2, and (*E*)-Q2, with greater dipole moments and



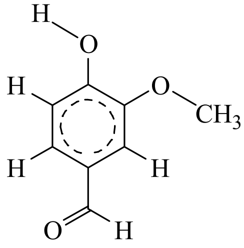
(*Z*)-B1



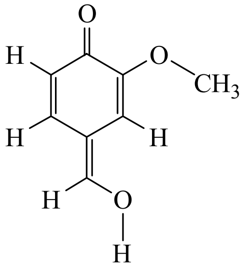
(*E*)-B1



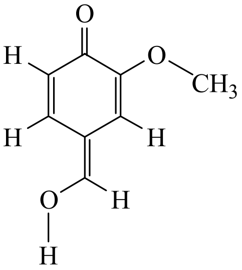
(*Z*)-B2



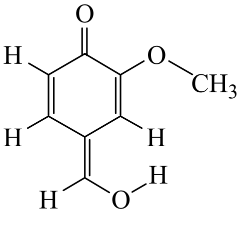
(*E*)-B2



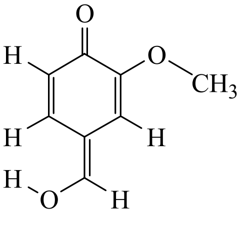
(*Z*)-Q1



(*E*)-Q1



(*Z*)-Q2



(*E*)-Q2

Table 1. The principal values of polarizability (α_{xx}, α_{yy}, α_{zz}), the average polarizability (α_{av}), optical anisotropy (δ^2), the module of the hyperpolarizability vector (|b|), its projection (b_μ) and the module of the dipole moment vector (|μ|), a.u.

Molecule	α_{xx}	α_{yy}	α_{zz}	α_{av}	δ^2, %	|b|	b_μ	|μ|
m-NA[a]	122	105	44	90	14	396	–374	2.19
$CHCl_3$	54	54	34	47	4	36	36	0.44
(*Z*)-B1	142	120	54	105	13	858	–851	1.14
(*E*)-B1	146	117	54	106	13	821	–387	2.02
(*Z*)-B2	141	123	54	106	13	891	–620	1.35
(*E*)-B2	144	120	54	106	13	823	–723	1.33
(*Z*)-Q1	176	111	55	114	19	388	56	2.90
(*E*)-Q1	178	109	55	114	19	61	51	2.99
(*Z*)-Q2	171	112	55	113	18	287	–61	2.07
(*E*)-Q2	173	111	55	113	18	57	44	1.99

[a] *m*-NA corresponds to *meta*-nitroaniline.

energies exceeding that of the form (*Z*)-B1 with its intramolecular hydrogen bond by 21.5–22.8 kcal mol^{-1} in a vacuum and 14.7–16.7 kcal mol^{-1} in aqueous solution.

In this paper, using the same quantum-chemical method B3LYP/cc-pVTZ and GAUSSIAN-03 software [6] we performed quantum-chemical calculations of the dipole polarizability tensors and first hyperpolarizebilities of the vanillin benzoid and *p*-quinoid forms.

The molecule polarizability is characterized by the principal values α_{xx}, α_{yy}, α_{zz} of the polarizability tensor $\boldsymbol{\alpha}$ with the average value $\alpha_{av} = 1/3\ (\alpha_{xx} + \alpha_{yy} + \alpha_{zz}) = 1/3 Spur(\boldsymbol{\alpha})$ and optical anisotropy $\delta^2 = 3||\boldsymbol{\alpha} - \alpha_{av}\,\mathbf{1}||^2/Spur^2(\boldsymbol{\alpha}) = [(\alpha_{xx} - \alpha_{yy})^2 + (\alpha_{xx} - \alpha_{zz})^2 + (\alpha_{yy} - \alpha_{zz})^2]/(\alpha_{xx} + \alpha_{yy} + \alpha_{zz})^2$. The value of δ^2 is manifested in the optical Kerr effect and Rayleigh light scattering [7].[1]

The first hyperpolarizability is completely symmetric third-rank tensor $\boldsymbol{\beta}$. Due to the molecule symmetry tensor contains no more than six different non-zero components (β_{xxx}, β_{yyy}, β_{xxy}, β_{xyy}, β_{xzz}, β_{yzz}). The $\boldsymbol{\beta}$ tensor convolution results in the vector **b** with the components: $b_x = \beta_{xxx} + \beta_{xyy} + \beta_{xzz}$; $b_y = \beta_{yyy} + \beta_{yxx} + \beta_{yzz}$; $b_z = 0$.

The module |**b**| characterizes the first hyper-polarizability value as a whole, and the projection $b_\mu = \mathbf{b}\cdot\boldsymbol{\mu}/|\boldsymbol{\mu}|$ of vector **b** on the direction of the dipole moment $\boldsymbol{\mu}$ is of interest in the discussion of nonlinear optical properties of a solution in a sufficiently strong external electric field. Sign of the projection b_μ determines the character of the dependence of the nonlinear optical properties of a polarized solution on the concentration of the solute with non-zero first hyperpolarizability, and this dependence may be not a monotonic one [8]. So, the difference in the b_μ signs of the solvent molecule and solute suggests that the efficiency of second harmonic generation by the solution with increasing concentration initially will decrease and then increase.

The above characteristics of the vanillin tautomers (Table 1) are invariant with respect to the rotation of the axes and the translation of the origin.

Calculations of wavelengths and oscillator strengths of allowed $\pi\rightarrow\pi^*$-transition in the electronic spectra of the tautomers of vanillin (Table 2)[2] indicate the absence of absorption bands in the visible region, that is, a sufficient transparency of vanillin at the prototropic tautomerism and at red shift solvation effects. The calculated spectra of benzoid forms are in satisfactory agreement with the experimental spectra of vanillin solutions [10, 11] and with the results of earlier semiempirical calculations [11, 12].

Table 3 complements the information on the spectral properties of the vanillin tautomers: it contains

---

[1] Checking calculation of the tensor polarizability of anthracene molecule gave the average polarizability α_{av} = 170 au = 25.2 Å^3, that is close to the experimental value 25.3 Å^3, and the optical anisotropy δ^2 = 26%, which is twice the experimental one (11%).

[2] Calculations were carried out by TD B3LYP/cc-pVTZ/PCM method. The cavity boundaries occupied by a molecule in a dielectric continuum are determined in the frameworks of PCM model [9] by the radii of spheres (C 1.925, CH 2.125, CH_3 2.525, O 1.75, and H_{ac} 1.443 Å) centered on the nuclei C, O, and H_{ac}, respectively.

Table 2. Wavelengths and oscillator strengths ($f > 0.004$) of allowed electronic transitions

Molecule	Wavelength, nm		Oscillator strength f		Molecule	Wavelength, nm		Oscillator strength f	
	vacuum	chloroform	vacuum	chloroform		vacuum	chloroform	vacuum	chloroform
(*Z*)-B1	284	296	0.139	0.212	(*Z*)-Q1	332	339	0.151	0.285
	257	265	0.155	0.196		281	292	0.337	0.354
	222	226	0.198	0.248		234	237	0.076	0.099
(*E*)-B1	285	300	0.139	0.189	(*E*)-Q1	347	357	0.146	0.243
	259	265	0.093	0.141		275	285	0.316	0.371
	221	226	0.335	0.431		235	238	0.121	0.159
(*Z*)-B2	293	303	0.117	0.187	(*Z*)-Q2	319	333	0.199	0.322
	256	264	0.157	0.212		281	291	0.261	0.289
	224	228	0.235	0.272		237	238	0.068	0.097
(*E*)-B2	295	307	0.117	0.168	(*E*)-Q2	351	359	0.145	0.231
	259	265	0.082	0.141		272	283	0.265	0.348
	222	228	0.397	0.469		238	239	0.158	0.182

Table 3. The wavelengths of the $n \rightarrow \pi^*$-transitions calculated by TD B3LYP/cc-pVTZ, nm

Molecule	Vacuum	Chloroform
(*Z*)-B1	325	319
(*E*)-B1	327	320
(*Z*)-B2	326	319
(*E*)-B2	327	320
(*Z*)-Q1	394	368
(*E*)-Q1	398	371
(*Z*)-Q2	389	366
(*E*)-Q2	396	371

calculated wavelengths of ($n \rightarrow \pi^*$)-transitions in the vicinity of the boundary between UV and visible spectral region, but of very low intensity and suffering a blue shift under the influence of polar solvent.

The transformation of benzoid tautomers into the *p*-quinoid ones slightly increases the average polarizability and the optical anisotropy of the vanillin molecule. The tautomeric transformations and conformational changes affect the vanillin hyperpolarizability even more (Table 1).

Benzoid tautomers exceed the *m*-nitroaniline molecule in hyperpolarizability. The hyperpolarizability of *p*-quinoid tautomers is lower than that of benzoid tautomers. On the other hand, *p*-quinoid tautomers possess relatively low ionization potential [5] and high electron affinity [5, 11]. Their formation as a result of topochemical proton transfer reaction between neighboring molecules along the hydrogen bonds in the crystal of vanillin can promote of the second harmonic generation of infrared laser radiation due to the appearance of supramolecular nanostructures (linear defects) with a high hyperpolarizability in the crystal lattice of low symmetry.

In contrast to the phase transition due to topochemical proton transfer occurring in the crystal of the salt formed by 4,4'-bipyridyl and squaric acid [13], the isomerization of vanillin in the crystal requires relatively high energy and obviously cannot end by the transition of the entire crystal into a new high-energy phase consisting of molecules of *p*-quinoid structure. Because of the difference in the color of the two phases, while heating to 180°C of the monoclinic form of salt Reetz et al. [13] succeeded to observe a movement of the boundary between the low-temperature yellow phase and the high-temperature red phase from one edge of the crystal to the opposite with the increase in the length of the modified chain segments of single charged squaric acid anions and pyridylpyridinium cations connected through the labile hydrogen atoms.

REFERENCES

1. Singh, O.P., Singh, Y.P., Singh, N., and Singh, N.B., *J. Cryst. Growth*., 2001, vol. 225, nos. 2–4, p. 470.
2. Davydov, B.L., Kotovshchikov, S.G., and Nefedov, V.A., *Kvantovaya Elektronika*, 1977, vol. 4, no. 1, p. 214.
3. *Nonlinear Optical Properties of Organic Molecules and Crystals*, Chemla, D.S. and Zyss, J., Eds., Moscow: Mir, 1989, vol. 1.
4. Velavan, R., Sureshkumar, P., Sivakumar, K., and Natarajan, S., *Acta Cryst. (C),* 1995, vol. 51, no. 6, p. 1131.
5. Semenov, S.G. and Makarova, M.V., *Zh. Obshch. Khim*., 2010, vol. 80, no. 9, p. 1487.
6. Frisch, M.J., Trucks, G.W., Schlegel, H.B., Scuseria, G.E., Robb, M.A., Cheeseman ,J.R., Montgomery, J.A., Jr.,

Vreven, T., Kudin, K.N., Burant, J.C., Millam, J.M., Iyengar, S.S., Tomasi, J., Barone, V., Mennucci, B., Cossi, M., Scalmani, G., Rega, N., Petersson, G.A., Nakatsuji, H., Hada, M., Ehara, M., Toyota, K., Fukuda, R., Hasegawa, J., Ishida, M., Nakajima, T., Honda, Y., Kitao, O., Nakai, H., Klene, M., Li, X., Knox, J.E., Hratchian, H.P., Cross, J.B., Adamo, C., Jaramillo, J., Gomperts, R., Stratmann, R.E., Yazyev, O., Austin, A.J., Cammi, R., Pomelli, C., Ochterski, J.W., Ayala, P.Y., Morokuma K., Voth, G.A., Salvador, P., Dannenberg, J.J., Zakrzewski, V.G., Dapprich, S., Daniels, A.D., Strain, M.C., Farkas, O., Malick, D.K., Rabuck, A.D., Raghavachari, K., Foresman, J.B., Ortiz, J.V., Cui, Q., Baboul, A.G., Clifford, S., Cioslowski, J., Stefanov, B.B., Liu, G., Liashenko, A., Piskorz, P., Komaromi, I., Martin, R.L., Fox, D.J., Keith, T., Al-Laham, M.A., Peng, C.Y., Nanayakkara, A., Challacombe, M., Gill, P.M.W., Johnson, B., Chen, W., Wong, M.W., Gonzalez, C., and Pople, J.A. *GAUSSIAN-03*, Rev. B.05. Pittsburgh PA: Gaussian, 2003.

7. Vereshchagin, A.N., *Polyarizuemost’ molekul* (Polarizability of Molecules), Moscow: Nauka, 1980.
8. Brotin, T., Andraud, C., Ledoux, I., Brasselet, S., Zyss, J., Perrin, M., Thozet, A., and Collet, A., *Chem. Mater.*, 1996, vol. 8, no. 4, p. 890.
9. Tomasi, J. and Persico, M., *Chem. Rev.*, 1994, vol. 94, no. 7, p. 2027; Tomasi, J., Mennucci, B., and Cammi, R., *Ibid.*, 2005, vol. 105, no. 8, p. 2999.
10. Rajendiran, N. and Balasubramanian, T., *Spectrochim. Acta, A*, 2008, vol. 69, no. 3, p. 822.
11. Semenov, S.G. and Shevchenko, S.M., *Khimiya drevesiny* (Chemistry of Wood), 1987, no. 1, p. 86; Semenov, S.G. and Shevchenko, S.M., *Chem. Papers*, 1991, vol. 45, no. 3, p. 289.
12. Semenov, S.G. and Khodyreva, N.V., *J. Mol. Struct. (Theochem.)*, 1995, vol. 337, no. 1, p. 89.
13. Reetz, M.T., Höger, S., and Harms, K., *Angew. Chem.*, 1994, vol. 106, no. 2, p. 193.