Electrostatic Properties of 3-(p-Ethoxyphenyl)sydnone *

Jumn-Min Fan, Yu Wang, and Chuen-Her Ueng
Department of Chemistry, National Taiwan University Taipei, Taiwan, ROC

Z. Naturforsch. **48a**, 105–108 (1993); received December 28, 1991

The bonding type and characteristic chemical reactions of the sydnone ring have been rationalized by examination of the deformation electron density distribution and electrostatic potential from both experiment and theory. The net atomic charges, bond lengths and bond orders of the title compound confirm the semiaromatic bonding type for the sydnone ring. The highly negative net atomic charge of C4 suggests its susceptibility to electrophilic substitution at this position. The well known 1,3-dipolar cycloaddition reaction of the sydnone ring can be understood by the analysis of the π-orbital wavefunctions, which give rise to similar deformation densities as the experimental ones. The good agreement between the experimental and theoretical (ab initio calculation using 3-21G basis sets) deformation density distribution of the title compound justifies the use of the same basis set to derive the electrostatic potential. The electrostatic potential map reveals all the possible protonation sites of the sydnone ring at O1, N2 and O6 with the deepest hole at O6 (84.6 kcal/mole).

Key words: Sydnone; Deformation charge density; Electrostatic potential.

The molecular structure of 3-(p-ethoxyphenyl)sydnone [1] is shown in Figure 1. The phenyl ring plane and the sydnone ring plane are nearly coplanar (dihedral angle of 2°). A deformation density study of this compound is presented here using both experimental X-ray diffraction data at 110 K and a split valence basis ab-initio calculation. The deformation densities examined are $\Delta\varrho_{\mathrm{X-X}}$, $\Delta\varrho_{\mathrm{m-a}}$, and $\Delta\varrho_{\mathrm{mo-ao}}$, where $\Delta\varrho_{\mathrm{X-X}}$ is from conventional X–X (high angle [2], $\Delta\varrho_{\mathrm{m-a}}$ is from a multipole model [3], $\Delta\varrho_{\mathrm{mo-ao}}$ is from an ab-initio calculation using a 3-21G basis set [4]. The bond lengths, bond orders and net atomic charges of this compound are presented in Table 1 with comparison between experimental and theoretical results. Bond lengths and bond orders indicate C5–O6 to be essentially a double bond with C5–O1, N2–O1 single bonds. As for the net atomic charge derived from the multipole model, N2 and N3 are neutral, C4, O1 and O6 are negative and C5 is positive; the calculated theoretical net atomic charges using Mulliken popula-

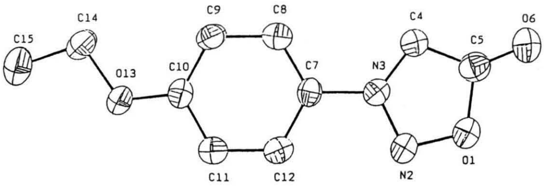

Fig. 1. Molecular drawing with thermal ellipsoids at 110 K.

Table 1. Bond lengths, bond orders and net atomic charges of the sydnone ring as part of 3-(p-ethoxyphenyl)sydnone (X-ray diffraction geometry).

Bond lengths (in Å)

O1–N2	N2–N3	N3–C4	C4–C5	C5–O6	C5–O1	N3–C7
1.379(1)	1.317(1)	1.345(1)	1.414(1)	1.224(1)	1.411(1)	1.345(1)

Bond orders (AM1)

O1–N2	N2–N3	N3–C4	C4–C5	C5–O6	C5–O1	N3–C7
1.178	1.375	1.164	1.156	1.804	0.787	0.926

Net atomic charges

	O1	N2	N3	C4
Multipole, $l=0$	−0.08(2)	0.02(2)	0.04(2)	−0.28(2)
AM1	−0.18	0.04	0.06	−0.39
ab-initio	−0.51	0.14	−0.75	−0.02

	C5	O6	C7	H(C4)
Multipole, $l=0$	0.19(2)	−0.26(2)	−0.13(2)	0.26(1)
AM1	0.32	−0.28	−0.03	0.22
ab-initio	0.81	−0.64	0.36	0.31

Multipole, $l=0$: multipole model (refined to monopole, $l=0$).

---

* Presented at the Sagamore X Conference on Charge, Spin and Momentum Densities, Konstanz, Fed. Rep. of Germany, September 1–7, 1991.

Reprint requests to Prof. Dr. Yu Wang, Department of Chemistry, National Taiwan University, Taipei, Taiwan, Republic of China.

0932-0784 / 93 / 0100-0105 $ 01.30/0. – Please order a reprint rather than making your own copy.

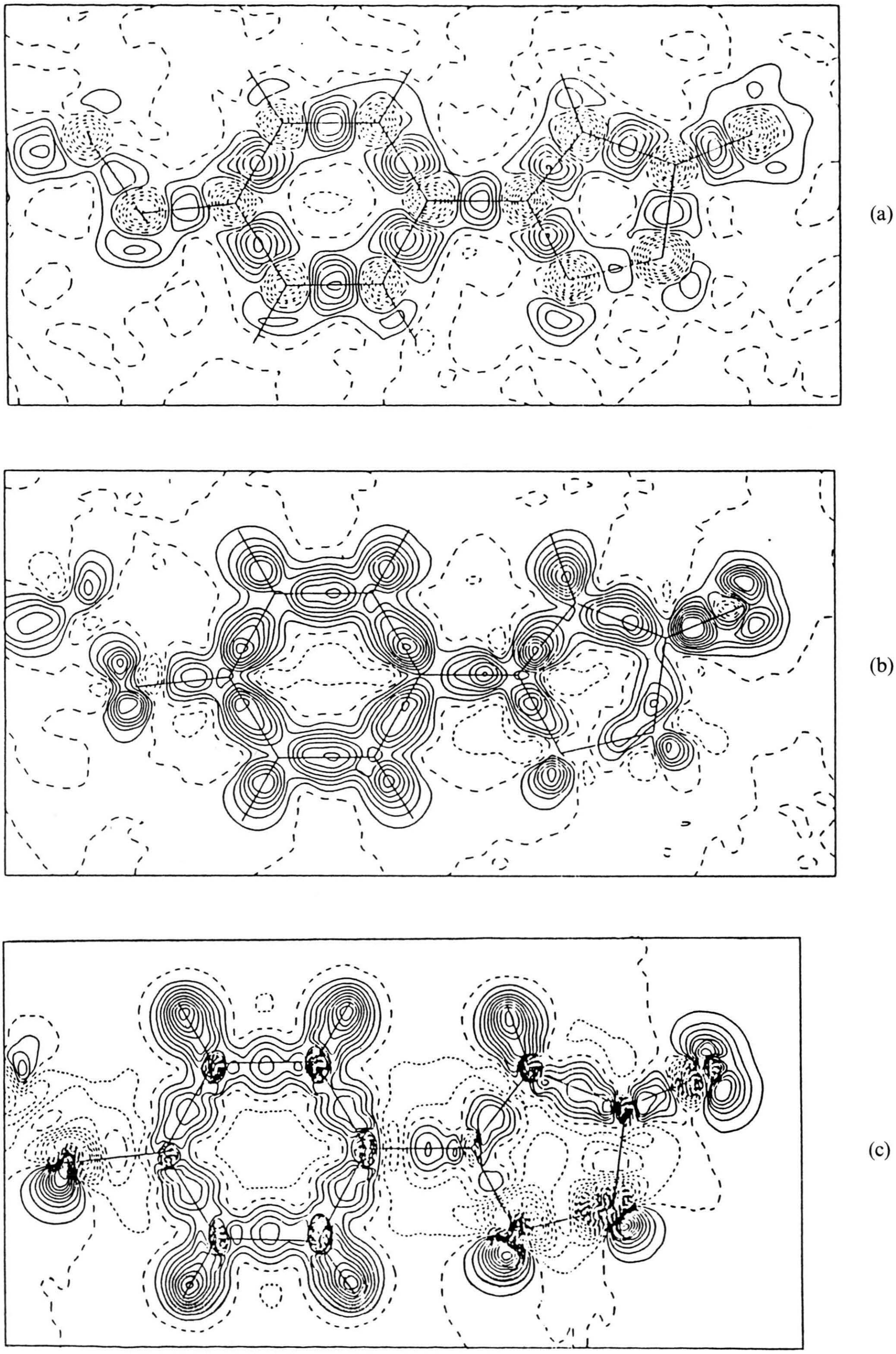

Fig. 2. Deformation density maps of 3-(p-ethoxyphenyl)sydnone through the C8–C7–N3 plane; solid lines positive, dashed and dotted lines zero and negative, respectively. Contour interval: 0.1 eÅ^{-3}. a) $\Delta\varrho_{X-X}$, b) $\Delta\varrho_{m-a}$, c) $\Delta\varrho_{mo-ao}$.

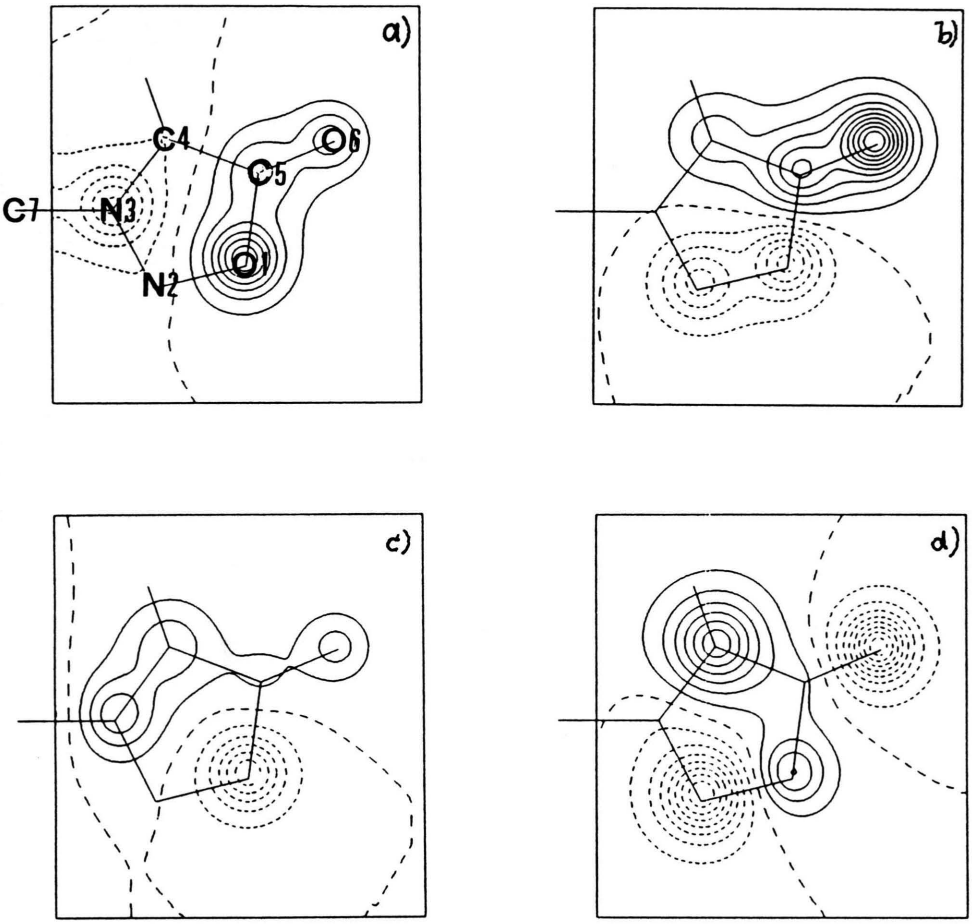

Fig. 3. Wave functions of the four occupied π-orbitals of the sydnone ring from the title compound; contours at the plane 0.5 Å above the sydnone plane. a) $\pi 1$: -0.58551 hartrees, b) $\pi 2$: -0.50555 hartrees, c) $\pi 3$: -0.48832 hartrees, d) $\pi 4$: -0.31595 hartrees (HOMO).

tion definition are also listed for comparison. All the theoretical results are based on the geometry obtained from the X-ray diffraction data. The deformation densities are shown in Figure 2. It is obvious that $\Delta\varrho_{\mathrm{X-X}}$, $\Delta\varrho_{\mathrm{m-a}}$, and $\Delta\varrho_{\mathrm{mo-ao}}$ are consistent. They show agreement not only along the bonding regions, but also around lone-pair regions. Because of the good agreement in Figs. 2b and 2c it is justified to use the orbital wavefunctions obtained from such an ab-initio calculation (3-21G basis set) for the analyses of the bonding type and of the possible chemical reactions. In order to understand the bonding type of the sydnone ring from this study, the wavefunctions of the p-π orbitals of the sydnone ring are analyzed. There are four occupied π-orbitals shown in Fig. 3, which conforms to the semiaromatic character [5]. The HOMO of the compound (Fig. 3d) has large coefficients on both C4 and N2 with opposite sign; this is in accord with the well-known 1,3-dipolar cycloaddition reaction [6] of the sydnone ring according to the frontier orbital consideration. The electrophilic substitution reaction at C4 can be rationalized with its high electron density (Table 1). In addition, the electrostatic potential $V(\boldsymbol{r})$ map [7] of the molecule can be derived in the same ab-initio calculation according to the definition

$$V(\boldsymbol{r}) = \sum_a \frac{Z_a}{|\boldsymbol{R}_a - \boldsymbol{r}|} - \int \frac{\varrho(\boldsymbol{r}')\,\mathrm{d}\boldsymbol{r}'}{|\boldsymbol{r}' - \boldsymbol{r}|},$$

where Z_a is the charge on nucleus a, located at $\boldsymbol{R}_a$, and $\varrho(\boldsymbol{r})$ is the electronic density function. The electrostatic

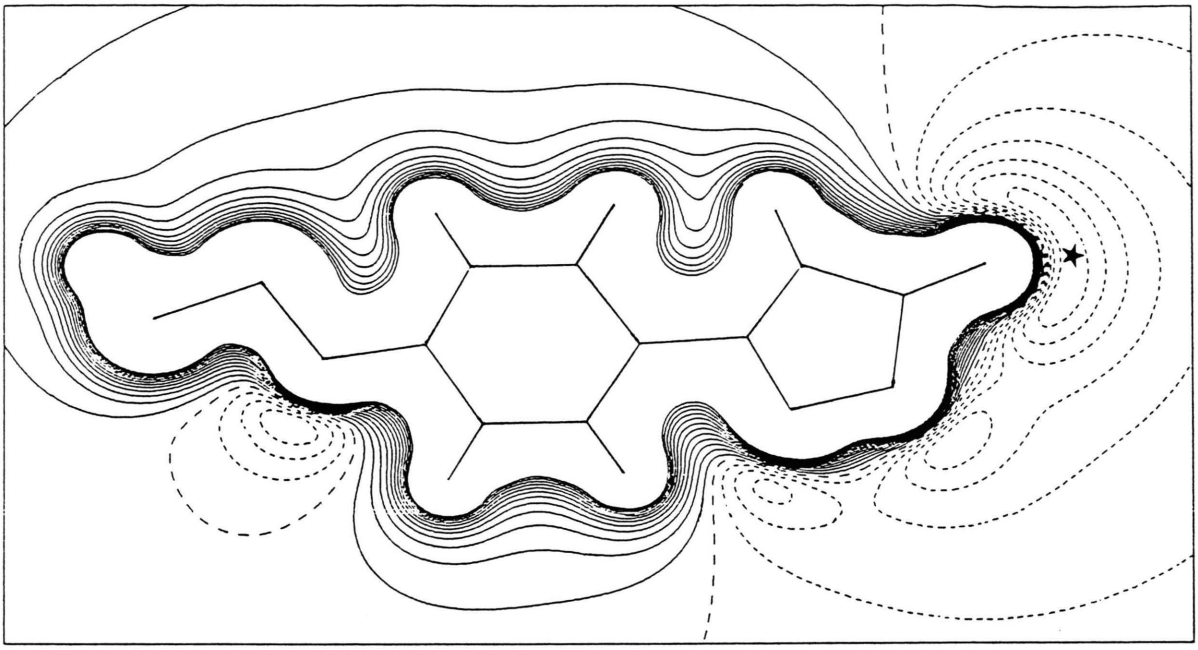

Fig. 4. Calculated electrostatic potential (kcal/mole) of 3-(p-ethoxyphenyl)sydnone, contour interval: 12.73 kcal/mole. The most negative potentials are indicated; ★: 84.6 kcal/mole.

potential map (Fig. 4) shows three negative regions around the sydnone ring near O1 (63.6 kcal/mole), N2 (50.9 kcal/mole) and O6 (84.6 kcal/mole). Considering that the process of protonation is started as a long-range electrostastic interaction [7], the negative regions of the potential should imply the probable protonation sites. In this case, the probable protonation sites around the sydnone ring are near O1, N2, and O6 with the deepest hole (84.6 kcal/mole) near O6. It suggests that the most probable protonated site is at O6, which is in accord with the heat-of-formation calculation of the protonated species [8].

[1] Y. Wang, P. L. Lee, and M. Y. Yeh, Acta Crystallogr. C **40**, 1226 (1984).

[2] P. Coppens and M. B. Hall (eds.), Electron Distributions and the Chemical Bond, Plenum Press, New York 1982.

[3] N. K. Hansen and P. Coppens, Acta Crystallogr. A **34**, 909 (1978).

[4] M. J. Frisch, M. Head-Gordon, H. B. Schlegel, K. Raghavachari, J. S. Binkley, C. Gonzalez, D. J. Defrees, D. J. Fox, R. A. Whiteside, R. Seeger, C. F. Melius, J. Baker, R. Martin, L. R. Kahn, J. J. P. Stewart, E. M. Fluder, S. Topiol, and J. A. Pople, Gaussian 90, Gaussian Inc., Pittsburgh, PA 1990.

[5] S. Nespurek, J. Hašek, M. Sorm, K. Huml, J. Obrda, J. Lipinski, and H. Chojnacki, J. Mol. Struct. **82,** 95 (1982).

[6] P. Krogsgaard-Larsen, L. Brehm, and K. Schaumburg, Acta Chem. Scand., Ser. B **35,** 311 (1981).

[7] P. Politzer and D. G. Truhlar (eds.), Chemical Applications of Atomic and Molecular Electrostatic Potentials, Plenum Press, New York, London 1981.

[8] M. Eckert-Maksić and Z. B. Maksić, J. Chem. Soc. Perkin II **1981,** 1462.