J. Phys. Chem. A **2003,** *107,* 8975−8979 **8975**

Hydrogen-Bonding Ability of a Methyl Group

Svend J. Knak Jensen,*,† Ting-Hua Tang,‡ and Imre G. Csizmadia§,||

Department of Chemistry, Langelandsgade 140, University of Aarhus, DK-8000, Aarhus C, Denmark,
Department of Chemistry, McMaster University, Hamillton, Ontario L8S 4M1, Canada, Lash Miller Chemical
Laboratories, 80 St. George Street, University of Toronto, Toronto, Ontario M5S 3H6, Canada, and
Department of Medical Chemistry, Szent Györgyi Medical Center, University of Szeged, Dóm tér 8,
H-6720 Szeged, Hungary

Received: April 16, 2003; In Final Form: July 28, 2003

Hydrogen bonds involving the methyl group have been studied by topological analysis of the electron density derived from quantum mechanical geometry-optimized structures of selected molecules/ions. The results indicate that hydrogen-bond formation not only depends on the distance from the methyl group to the proton acceptor, X, but also on the angle CH···X. The species investigated suggest the angle should be bigger than about 100° for hydrogen-bond formation.

1. Introduction

The strength of a hydrogen bond depends on the acidity of the proton donor (H−A) and the basicity of the proton acceptor (X:).

$$X{:}\cdots\cdot H{-}A \qquad (1)$$

Carbon-acids ($R_1R_2R_3C{-}H$) are very weak acids ($40 < pK_a < 50$) and, apart from some recent and important investigations,[1−5] most studies of hydrogen bonding have considered the hydrocarbons to be too weak proton donors for hydrogen-bond formation. This has been the case in both chemistry and biology. For example, the biochemical description of protein folding includes a phase called *hydrophobic collapse* in which the amino acids assume conformations which result in an arrangement whereby all hydrocarbon side-chains move toward the central core of the *molten globule* stage of a protein.[6] This implies that these hydrocarbon side-chains are held together to avoid the aqueous phase, but there is no consideration of a potential hydrogen bond to, e.g., the carbonyl of a peptide bond

$$^{>N}{>}C{=}O\cdots\cdot H{-}CR_1R_2R_3 \qquad (2)$$

Biomolecules are very flexible and it is difficult to separate hydrogen-bonding energies from conformational energy changes. We considered it to be prudent to initiate our study with the use of some rigid system in which the relative stability of the hydrogen bonds may be more clearly assessed. In view of that, we have chosen to study *o*-tolyl derivatives with various proton acceptors, i.e., the isoelectronic toluenes *o*-$CH_3{-}C_6H_4{-}O_2^-$, *o*-$CH_3{-}C_6H_4{-}O_2H$, and *o*-$CH_3{-}C_6H_4{-}OF$. This choice reflects the expectation that negatively charged species are more basic than their neutral counterpart. Like:

$$-O^- > -OH \qquad (3)$$

and that the −OH group is a stronger proton acceptor than the −F group. Thus, if there is a hydrogen bond in these species, its strength is expected to decrease in the series. To explore the importance of geometry constraints, we have also studied two closely related sets of species with less rigidity for hydrogen-bond formation, i.e., *o*-$CH_3{-}C_6H_4{-}CH_2O^-$, *o*-$CH_3{-}C_6H_4{-}CH_2OH$, and *o*-$CH_3{-}C_6H_4{-}CH_2F$ as well as a set of *n*-alkylperoxy anions, $CH_3{-}(CH_2)_n{-}O_2^-$, $n = 0, 1, 2, 3$.

The article is organized as follows: In Section 2 we list the theoretical methodologies used. In Section 3 we present our findings, which are discussed in Section 4. The Summary is found in Section 5.

2. Theoretical Details

2.A. Geometry Determinations. The equilibrium geometry of the various molecules and ions considered are determined by quantum mechanical geometry optimizations using the density functional theory (DFT)[7] as implemented in the GAUSSIAN98 package.[8] The correlation correction by Lee, Yang, and Parr (LYP)[9] together with Becke's nonlocal, gradient approach to the exchange functional in its three parameter hybrid density form (B3LYP)[10] has been used. Ab initio geometry optimizations are also performed using the Møller−Plesset method (MP2). The split-valence basis set 6-311++G(d,p) with diffuse functions on all atoms[8,11] is employed in the bulk of the calculations. However, larger and smaller basis sets, including Dunning's correlation-consistent augmented basis set,[12] AUG-cc-pVDZ, are also used for comparison.

2.B. Topological Properties Analysis. The topological properties analysis of the electron density distributions is based on the theory of atoms in molecules (AIM).[13] The total electron density, $\rho(\mathbf{r})$, is calculated from the wave function of the determined equilibrium geometry. The topological properties of $\rho(\mathbf{r})$ are characterized by its critical points (CPs) when $\nabla\rho(\mathbf{r}) = 0$. According to the AIM theory, the bond critical points (BCPs) and bond paths (BPs) of electron density can be used to construct a molecular graph representing the network of BPs (i.e., a set of BPs) to connect bonded atoms. The existence of a BCP at $r = r_b$ between two atoms is the necessary condition for creating a BP, where the BP is "a universal indicator of bonded interactions".[14] The network of BPs therefore represents

---

* Corresponding author. Phone: +(45) 8942 3862. Fax: +(45) 8619 6199. E-mail: kemskj@chem.au.dk.

† University of Aarhus.

‡ McMaster University.

§ University of Toronto.

|| University of Szeged.

10.1021/jp035024h CCC: $25.00

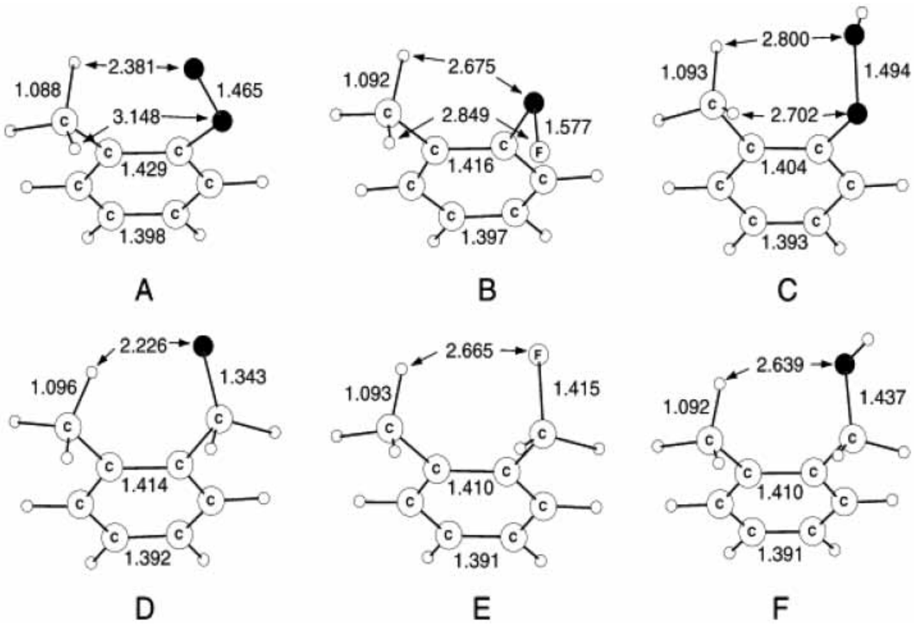

Figure 1. Structures of the various molecules and ions investigated at the B3LYP/6-311++G(d,p) level of theory. Arrows indicate the potential hydrogen bonds in Å. ● and ○ denote an oxygen atom and a hydrogen atom, respectively. A: *o*-$CH_3-C_6H_4-O_2^-$, B: *o*-$CH_3-C_6H_4-OF$, C: *o*-$CH_3-C_6H_4-O_2H$, D: *o*-$CH_3-C_6H_4-CH_2O^-$, E: *o*-$CH_3-C_6H_4-CH_2F$, F: *o*-$CH_3-C_6H_4-CH_2OH$.

all atomic interactions in a given system. The same bond critical points define a unique line in the electron density, which links the nuclei of neighboring atoms. It is called a bond path. A bond path is not necessarily coincident with the internuclear axis and when it is not, the length (BP) along the bond path is longer than the geometrical bond length (BL). The AIM theory is extensively used for the determination of hydrogen bonding.[15−18] The electron density at the BCP, ρ_b, is related to the bond strength or the bond order.[19−21] The sign of the Laplacian of ρ at the BCP, $\nabla^2\rho_b$, may be used to distinguish bonding type between the shared interaction (covalent bond) and the closed-shell interaction (e.g., ionic bond).

The topological properties associated with the BCP, maps of the charge density distributions, and Laplacian distributions are analyzed with the programs AIMPAC[22]/AIM98PC.[23]

3. Results

3.A. Geometry Optimizations. *3.A.1. Ortho-Substituted Toluenes*. The peroxyphenyl anion is found to have a planar C_s symmetry. Calculations indicate that the activation energy for rotation of the O_2^- moiety is about 46 kJ/mol at the B3LYP/6-311++G(d,p) level. When a methyl group is placed in the position ortho to the peroxy group the resulting ion will exhibit cis/trans isomerism. The trans isomer is the more stable by 25.7 kJ/mol (B3LYP/6-311++G(d,p)). At a low level of theory, i.e., HF/6-31G*, the structure of the cis isomer is close to having the phenyl ring as a symmetry plane with the terminal oxygen atom chelated by two H atoms of the methyl group in just about the same distance. As the level of theory increases, the difference between these two distances increases. In Table 1 we list the distances as a function of the level of theory along with distance between the terminal oxygen atom and the C atom of the methyl group. It appears that the variation of the length of the potential hydrogen bonds is much larger than that of the C−O distance. Thus, a large basis set is needed to investigate the hydrogen bonding in this type of compounds. Likewise, the structure of $C_6H_5-O_2H$ is close to being planar. The activation energy for rotation of the O_2H group is estimated to be 5.5 kJ/mol, and when a methyl group is substituted in the ortho position the trans isomer becomes 3.8 kJ/mol more stable than the cis isomer. In the following we will only be concerned with the cis isomers of *o*-$CH_3-C_6H_4-O_2^-$ and *o*-$CH_3-C_6H_4-O_2H$.

TABLE 1: Variation of Selected Distances in *o*-$CH_3-C_6H_4-O_2^-$ with the Level of Theory[a]

level of theory	R($H_1\cdots O$) (Å)	*R*($H_2\cdots O$) (Å)	*R*($C\cdots O$) (Å)
HF/6-31G*	2.515	2.527	2.744
B3LYP/6-31+G(d,p)	2.445	2.600	2.759
B3LYP/AUG-cc-pVDZ	2.484	2.552	2.751
B3LYP/6-311++G(d,p)	2.381	2.671	2.762
MP2/6-311++G(d,p)	2.432	2.578	2.733
MP2/6-311+G(2d,2p)	2.413	2.550	2.709

[a] *R*($H_1\cdots O$) and *R*($H_2\cdots O$) are the two shortest distances between the terminal oxygen atom and the H atoms in the methyl group. *R*($C\cdots O$) is the distance between the terminal oxygen atom and the C atom of the methyl group.

Phenyloxyfluoride (isoelectronic with the peroxyphenyl anion) has a nonplanar C_s symmetry with the OF moiety in a plane normal to the phenyl ring. The energy requirement to bring the OF moiety into the plane of the phenyl ring is about 13 kJ/mol. There is no cis/trans isomerism when a methyl group is substituted in the ring of phenyloxyfluoride. In Figure 1 we show the structures of the various species with an indication of the possible hydrogen bonds. The potential hydrogen bond may be considered to be part of a polygon, which is not in the plane of the phenyl ring. We note that replacement of the middle oxygen atom with a CH_2 group leads to a shortening of the potential hydrogen bond.

3.A.2. n-Alkylperoxy Anions. We have determined equilibrium structures of $CH_3-(CH_2)_n-O_2^-$ for $n = 0, 1, 2, 3$ at the B3LYP/6-311++G(d,p) level of theory. There are several conformers of these species. However, we have concentrated on finding conformers which are likely to have an intramolecular hydrogen bond. The structures are shown in Figure 2.

3.B. Topological Analysis. *3.B.1 Ortho-Substituted Toluenes.* The molecules *o*-$CH_3-C_6H_4-O_2H$ and *o*-$CH_3-C_6H_4-OF$ have two electronegative atoms, which, in principle, may participate in hydrogen bonding. However, the AIM analysis shows no

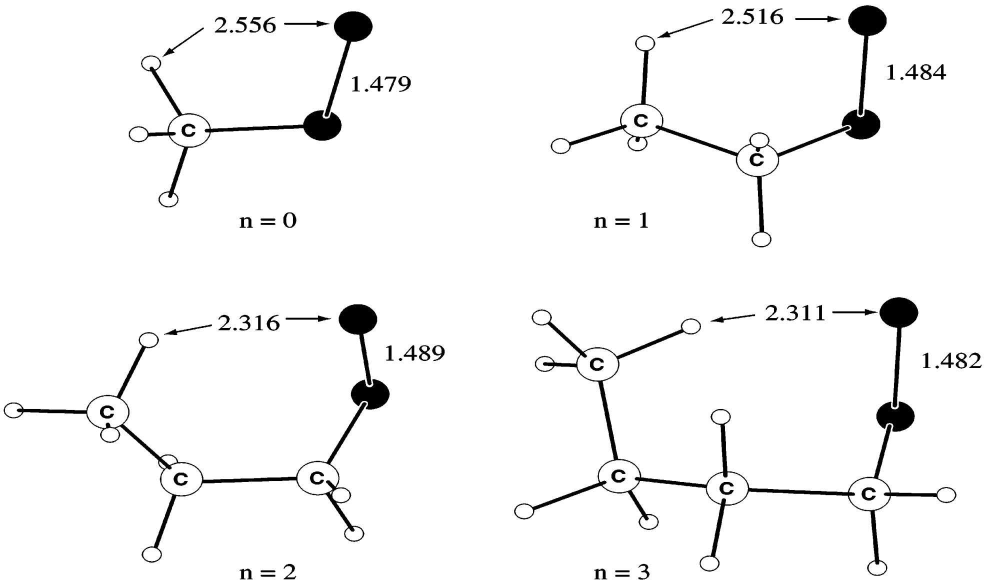

Figure 2. Structures of $CH_3-(CH_2)_n-O_2^-$ for $n = 0, 1, 2, 3$ calculated at the B3LYP/6-311++G(d,p) level of theory. The symbols are explained in Figure 1.

TABLE 2: Results of the Topological Analysis of the Wave Functions for the Structures A, D, E, and F Shown in Figure 1[a]

species	d_1 (Å)	d_2 (Å)	ρ_b (au)	$\nabla^2\rho_b$ (au)	BP (Å)	BL (Å)	∠CH···X (deg)
A: o-$CH_3-C_6H_4-O_2^-$	1.309	1.382	0.0170	0.0615	2.691	2.381	98.6°
	(- - -)	(- - -)	(- - -)	(- - -)	(- - -)	(2.484)	(92.1°)
	[- - -]	[- - -]	[- - -]	[- - -]	[- - -]	[2.432]	[94.0°]
B: o-$CH_3-C_6H_4-OF$	- - -	- - -	- - -	- - -	- - -	2.675	87.9°
	- - -	- - -	- - -	- - -	- - -	2.849	102.5°
	(- - -)	(- - -)	(- - -)	(- - -)	(- - -)	(2.692)	(87.5°)
	(- - -)	(- - -)	(- - -)	(- - -)	(- - -)	(2.850)	(101.9°)
	[- - -]	[- - -]	[- - -]	[- - -]	[- - -]	[2.610]	[92.1°]
	[- - -]	[- - -]	[- - -]	[- - -]	[- - -]	[2.813]	[95.1°]
C: o-$CH_3-C_6H_4-O_2H$	- - -	- - -	- - -	- - -	- - -	2.702	88.7°
	- - -	- - -	- - -	- - -	- - -	2.800	99.2°
	(- - -)	(- - -)	(- - -)	(- - -)	(- - -)	(2.672)	(90.3°)
	(- - -)	(- - -)	(- - -)	(- - -)	(- - -)	(2.717)	(97.1°)
	[- - -]	[- - -]	[- - -]	[- - -]	[- - -]	[2.647]	[92.0°]
	[- - -]	[- - -]	[- - -]	[- - -]	[- - -]	[2.776]	[94.1°]
D: o-$CH_3-C_6H_4-CH_2O^-$	0.886	1.363	0.0184	0.0558	2.248	2.226	127.0°
	(0.886)	(1.375)	(0.0180)	(0.0478)	(2.284)	(2.257)	(124.6°)
	[0.872]	[1.388]	[0.0167]	[0.0563]	[2.286]	[2.257]	[128.2°]
E: o-$CH_3-C_6H_4-CH_2F$	1.224	1.495	0.0069	0.0297	2.880	2.665	107.6°
	(1.210)	(1.504)	(0.0068)	(0.0316)	(2.872)	(2.659)	(108.0°)
	[1.153]	[1.457]	[0.0072]	[0.0326]	[2.704]	[2.585]	[112.2°]
F: o-$CH_3-C_6H_4-CH_2OH$	1.130	1.524	0.0085	0.0293	2.733	2.639	110.3°
	(1.133)	(1.528)	(0.0080)	(0.0302)	(2.740)	(2.647)	(110.8°
	[1.099]	[1.505]	[0.0086]	[0.0321]	[2.671]	[2.594]	[114.3°]

[a] Geometry data for the structures B and C, which do not have a BCP pertaining to a hydrogen bond, are also included. The data were obtained at the B3LYP/6-311++G(d,p), the B3LYP/AUG-cc-pVDZ, and the MP2/6-311++G(d,p) levels of theories with the results from the latter two given in parentheses () and [], respectively. d_1 and d_2 are the distances from the BCP to the H atom and electronegative atom, X, respectively. BL is the length of the (potential) hydrogen bond and BP is the length along the bond path. Two values are given for B and C. They refer to two potential hydrogen bonds, see Figure 1. ρ_b and $\nabla^2\rho_b$ are the electron density at the BCP and the Laplacian of the electron density at the BCP, respectively.

evidence for a BCP pertaining to a hydrogen bond for any of them at any level of theory up to MP2/6-311++G(d,p) and B3LYP/6-311++G(d,p). B3LYP calculations on o-$CH_3-C_6H_4-OF$ with a more extensive basis set, 6-311+G(2d,2p), also fail to lead to a BCP for a hydrogen bond. This suggests that the absence of a hydrogen bond is unlikely to be related to the size of the basis set.

The results in the case of o-$CH_3-C_6H_4-O_2^-$ vary with the level of theory. DFT calculations lead to a normal hydrogen bond in the case of the basis set 6-311++G(d,p). For other basis sets, the bond path is linked to the C atom of the methyl group. We speculate that the reason for this variation is that the electron density is very flat around the involved C and H atoms. This could make minor structural variations with the level of theory the deciding factor in the termination of the bond path.

We find a hydrogen bond in all the species: o-$CH_3-C_6H_4-CH_2O^-$, o-$CH_3-C_6H_4-CH_2OH$, and o-$CH_3-C_6H_4-CH_2F$. Details of the BCPs for the hydrogen bonds are listed in Table 2 along with some geometry parameters. It appears from Table 2 that the strength of the hydrogen bond in o-$CH_3-C_6H_4-CH_2O^-$, as measured by ρ_b, is stronger than the one in o-$CH_3-C_6H_4-O_2^-$. Also, the hydrogen bonds in the anions are stronger

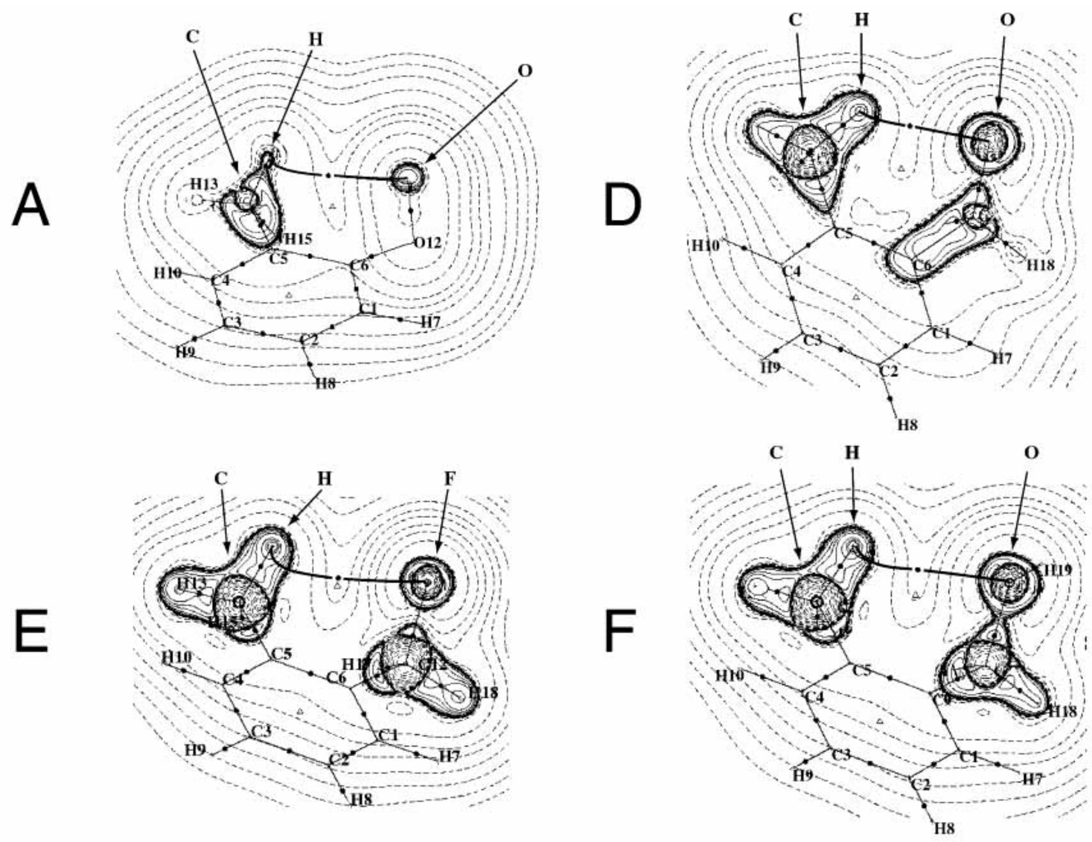

Figure 3. Contour maps of $\nabla^2\rho$ for the structures A, D, E, and F shown in Figure 1. The Laplacian has been calculated at the B3LYP/6-311++G-(d,p) level of theory. ● and △ indicate a bond critical point and a ring critical point, respectively. The bond path pertaining to the hydrogen bond is indicated with a heavy line. The arrows point to the three atoms (CH−X, X = O, F) involved in the hydrogen bond. These three atoms define the plane of the figure.

TABLE 3: Results of the Topological Analysis of the Wave Functions for the Species $CH_3-(CH_2)_n-O_2^-$ Shown in Figure 2[a]

$CH_3-(CH_2)_n-O_2^-$	d_1 (Å)	d_2 (Å)	ρ_b (au)	$\nabla^2\rho_b$ (au)	BP (Å)	BL (Å)	∠CH···X (deg)
$n = 0$	-	-	-	-	-	2.556	63.9°
$n = 1$						2.516	99.8°
$n = 2$	0.912	1.409	0.0160	0.0484	2.350	2.316	121.2°
$n = 3$	0.893	1.422	0.0144	0.0445	2.329	2.311	140.1°

[a] Geometry data for the structures with $n = 0$ and $n = 1$, which do not have a BCP pertaining to a hydrogen bond, are also included. The data were obtained at the B3LYP/6-311++G(d,p) level of theory. The symbols are explained in Table 2.

than the ones in the neutral species. Moreover, the Laplacian is positive in all cases which points to the ionic character of the bond. In Figure 3, we show plots of the Laplacian of the electron density of the four species with a BCP pertaining to a hydrogen bond. It appears that the bond path is curved in all cases which is consistent with

$$\mathrm{BP} > \mathrm{BL} \tag{4}$$

3.B.2. n-Alkylperoxy Anions. The AIM analysis does not lead to a BCP pertaining to a hydrogen bond for the anions $CH_3-O_2^-$ and $CH_3-CH_2-O_2^-$. In contrast, there is a hydrogen bond for the larger ions $CH_3-C_2H_4-O_2^-$ and $CH_3-C_3H_6-O_2^-$. The topological details are presented in Table 3 along with some geometry parameters.

4. Discussion

Clearly the six ortho toluenes have a variety of hydrogen-bond strengths as measured by ρ_b

$$\mathrm{D} > \mathrm{A} > \mathrm{F} > \mathrm{E} \gg \mathrm{B, C} \tag{5}$$

The strongest are the negatively charged. The neutral $-CH_2Z-$substituted structures are considerably weaker, and B and C show no sign of hydrogen bonding at the levels of theory investigated. It is interesting to note that the length of the potential hydrogen bond in B is merely 0.01Å longer than the one in E. This illustrates that the distance is not the only parameter of importance for hydrogen-bond formation.

The plots in Figure 3 show that the bond paths are curved, and that the inequality [eq 4] holds. Figure 3 also suggests that the distance between the bond critical point and the ring critical point decreases as the hydrogen bond becomes weaker, this is in agreement with the expectation that the ring critical point collapses if the hydrogen bond disappears.

The α-effect suggests that oxygen lone pairs in Z−O−O−H functional groups are more nucleophilic than oxygen lone pairs in $Z-CH_2-OH$. This would suggest that $Z-CH_2-OH$ would be a weaker proton acceptor. The current observation suggests that either the α-effect is not dominant in hydrogen-bond formation or it is overridden by other factors.

The absence of a BCP in the cases B and C raises the question of how weak a bond can be detected by the AIM method. Molecules with weak interactions have been investigated before with the AIM method[24] and it was found, for example, that ρ_b

for Ar_2—calculated from a triple split basis set—was 0.0029 while the bond strength and bond length are about 1.0 kJ/mol and 3.9 Å, respectively.[25] This suggests that the threshold for detection of a weak hydrogen bond is below 1 kJ/mol.

On the other hand, a short distance of a potential hydrogen bond provides no guarantee for the actual existence of a hydrogen bond as is apparent from Tables 2 and 3. For example, the potential hydrogen-bond lengths for $CH_3-O_2^-$ and $CH_3-CH_2-O_2^-$ are shorter than the actual bond length for the species E and F in Table 2. The data in Tables 2 and 3 suggest that the relative orientation of a CH fragment and the electronegative atom X—as measured by the angle $\angle CH\cdots X$—is of importance. Thus, all the species in Tables 2 and 3 which exhibit a hydrogen bond have $\angle CH\cdots X$ larger than 98.6°, while all the species which do not have a hydrogen bond have $\angle CH\cdots X$ smaller than 101.9°. This suggests that a value for $\angle CH\cdots X$ around 100° represents a threshold for hydrogen-bond formation.

The AIM results for o-$CH_3-C_6H_4-CH_2O^-$ vary qualitatively with the level of theory. We consider this variation to reflect that at most levels of theory $\angle CH\cdots O$ happens to be below the threshold value. Referring to the data for this species we note that ρ_b is not small in the case B3LYP/6-311++G(d,p), where $\angle CH\cdots O$ is close to the threshold value. Thus ρ_b does not seem to vanish when $\angle CH\cdots O$ approaches the threshold value from above, but rather behaves like the order parameter in a first-order phase transition. Experimental support for the directionality of the CH···O bond has been reported in a study of trihydrate orthoamide, where an unexpected orientation of a CH_3 group 'is attributed to a CH···OH bonding, which must be much stronger and more directionally specific than has been previously assumed'.[26] The $\angle CH\cdots O$ angle associated with a hydrogen bond in trihydrate orthoamide is 170°.

In some cases,[3] a group of similar species exhibit a linear relationship between ρ_b and the strength of hydrogen bond, especially if the range of ρ_b is not too large. We will use this relationship to estimate the strength in kJ/mol of an intramolecular hydrogen bond involving the methyl group in the case of o-$CH_3-C_6H_4-CH_2O^-$. We assume o-$CH_3-C_6H_4-CH_2O^-$ and o-$HO-C_6H_4-COOH$ are "sufficiently similar" and use the experimental value,[27] 17.8 kJ/mol, for the strength of the intramolecular hydrogen bond in the latter species to estimate the strength in the former. The AIM analysis of the wave function for the optimized structure (B3LYP/6-311++G(d,p)) of o-$HO-C_6H_4-COOH$ leads to $\rho_b = 0.0183$ au which is very close to the $\rho_b = 0.0184$ au value for o-$CH_3-C_6H_4-CH_2O^-$ listed in Table 2. Thus we estimate that the intramolecular hydrogen bond in o-$CH_3-C_6H_4-CH_2O^-$ is about 18 kJ/mol.

5. Summary

The topological analysis of the electron density of six ortho-substituted toluenes and four n-alkylperoxy anions suggests that the methyl group can participate in hydrogen bonding if the angle from the CH moiety to the electronegative atom is larger than about 100°.

Acknowledgment. This work was supported by Grant (HDW-1101-14) from the Danish Center for Scientific Computing. One of us (I.G.C.) thanks the Hungarian Ministry of Education for the award of a Szent Györgyi Visiting Professorship.

References and Notes

(1) Sosa, G. L.; Peruchena, N. M.; Contreras, R. H.; Castro, E. A. *J. Mol. Struct. (THEOCHEM)* **2002**, *577*, 219.

(2) Rozas, I.; Alkorta, I.; Elguero, J. *J. Phys. Chem. A* **2001**, *105*, 10462.

(3) Grabowski, S. J. *J. Phys. Chem. A* **2000**, *104*, 5551.

(4) Steiner, T. *J. Phys. Chem. A* **2000**, *104*, 433.

(5) Steiner, T.; Desiraju, G. R. *Chem. Commun.* **1998**, 891.

(6) Voet, D.; Voet, J. G.; Pratt, C. W. *Fundamentals of Biochemistry*; Wiley: New York, 1999; p 153.

(7) Hohenberg, P.; Kohn, W. *Phys. Rev.* **1964**, *B136*, 864; (b) Kohn, W.; Sham, S. J. *Phys. Rev.* **1965**, *A140*, 1133; (c) Parr, R. G.; Yang, W. *Density-Functional Theory of Atoms and Molecules*; Oxford University Press: Oxford, U.K., 1989.

(8) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M, C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzales, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian98*, Revision A.6; Gaussian, Inc.: Pittsburgh, PA, 1998.

(9) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev.* **1988**, *B37*, 785.

(10) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.

(11) Francl, M. M.; Pietro, W. J.; Hehre, W. J.; Binkley, J. S.; Gordon, M. S.; DeFrees, D. J.; Pople, J. A. *J. Chem. Phys.* **1982**, *77*, 3654.

(12) Dunning, T. H., Jr. *J. Chem. Phys.* **1989**, *90*, 1007.

(13) Bader, R. F. W. *Atoms in Molecules: A Quantum Theory*; Clarendon Press: Oxford, U.K., 1990.

(14) Bader, R. F. W. *J. Phys. Chem*. **1998**, *A102*, 7314.

(15) Whitfield, D. M.; Tang, T.-H. *J. Am. Chem. Soc.* **1993**, *115*, 9648.

(16) Koch, U.; Popelier, P. L. A. *J. Phys. Chem*. **1995**, *99*, 9747.

(17) Whitfield, D. M.; Lamba, D.; Tang, T.-H.; Csizmadia, I. G. *Carbohydr. Res.* **1996**, *286*, 17.

(18) Platts, J. A.; Howard, S. T.; Bracke, B. R. F. *J. Am. Chem. Soc.* **1996**, *118*, 2726.

(19) (a) Bader, R. F. W.; Tang, T.-H.; Tal, Y.; Biegler-König, F. W. *J. Am. Chem. Soc.* **1982**, *104*, 940, 946. (b) Bader, R. F. W.; Slee, T.; Cremer, D.; Kraka, E. *J. Am. Chem. Soc.* **1983**, *105*, 5061.

(20) Kraka, E.; Cremer, D. In *The Concept of the Chemical Bond, Theoretical Models of Chemical Bonding*, Part 2; Makić, Z. B., Ed.; Springer-Verlag: New York, 1990.

(21) Cremer, D.; Kraka, E. *Croatica Chem. Acta* **1984**, *57*, 1259.

(22) Bader, R. F. W., and co-workers. *AIMPAC*: *A set of programs for the theory of atoms in molecules*; McMaster University: Hamilton, Ontario, Canada L8S 4M1, 1994.

(23) Fang, D.-C.; Tang, T.-H. *AIM98PC*. The modified PC version of AIMPAC, 1998.

(24) Bone, R. G. A.; Bader R. F. W. *J. Phys. Chem.* **1996**, *100*, 10892.

(25) Hirschfelder, J. O.; Curtis, C: F.; Bird, R. B. *Molecular Theory for Gases and Liquids*; Wiley/Chapman and Hall: New York/London, 1954.

(26) Seiler, P.; Dunitz, J. D. *Helv. Chim. Acta* **1989**, *72*, 1125.

(27) Sabbah, R.; Gouali M. *Thermochim. Acta* **1997**, *303*, 107.