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CNDO/2 Analyses of the Order of Protonation of Rodlike Polybenzobisoxazoles (PBO)

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Summary

Protonation of the rodlike polybenzobisoxazoles (PBO) and polybenzobisthiazoles and their model compounds in acidic media will have significant effects on their solubility, solution behavior, geometry, and conformational characteristics. Experimental studies on the *cis*-PBO model compound suggest that the aromatic heterocyclic group can accept up to four acidic protons, first at each of the two nitrogen atoms then at the two oxygen atoms. In this study geometry-optimized CNDO/2 calculations were carried out on the *cis*-PBO model compound to determine the order of successive protonation, estimate differences in proton binding energies, and provide information on the effects of successive protonation on the geometry and charge distribution. The results indicate that protonation occurs in the order nitrogen, nitrogen, oxygen, oxygen, which is consistent with the greater bascity of nitrogen relative to oxygen. The difference in energy between initial protonation at nitrogen versus oxygen is *ca.* 60.7 kcal mol^{-1}. Second protonation is preferred at the other nitrogen rather than at the more distant oxygen by nearly the same amount, suggesting that energetically the initial protonation at the nitrogen has a negligible effect on subsequent protonation and that the two oxazole moieties are highly insulated from each other. Repulsive Coulombic interactions between the acidic protons have a negligible influence on whether the second protonation occurs at the nitrogen or the oxygen considered. Coulombic effects will in fact slightly favor at the nitrogen since, despite its closer proximity to the nitrogen first protonated, protonation there yields a more delocalized and hence less repulsive charge distribution than at the oxygen.

Introduction

The rodlike polybenzobisoxazoles (PBO) and polybenzobisthiazoles are high-performance polymers since films and fibers processed from these materials exhibit high strength, good thermo-oxidative stability, and resistance to most common solvents (ARNOLD, 1979; HELMINIAK, 1979; WELSH, et al., 1981, 1982; WOLFE, et al., 1979; WONG, et al., 1977). The only materials found suitable as solvents for these materials are very strong acids such as chlorosulfonic acid, methanesulfonic acid, and polyphosphoric acid. Recent experimental and theoretical studies have focused on the behavior of these polymers in acidic media in order to provide information regarding their solubility characteristics and solution properties. In most cases the studies have been applied to small model compounds such as

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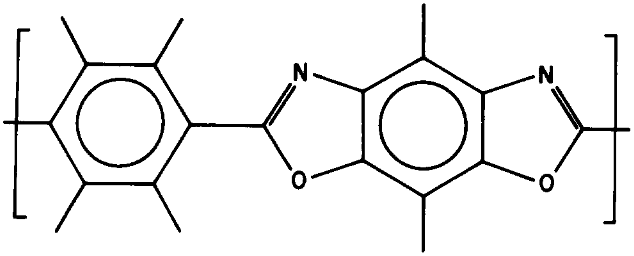

for the cis-PBO. (In the trans isomer a nitrogen and oxygen within the same oxazole ring switch places.) Some of these studies (BERRY, 1981; THOMAS, et al., 1980) have indicated that with increasing acidity the cis-PBO model compound can exist in the $2H^+$-form, with one acidic proton binding to each nitrogen atom, or in the $4H^+$-form, with the two additional protons binding to the two oxygen atoms. Both spectroscopic (THOMAS, et al., 1980) and theoretical (WELSH, et al., 1982) evidence have provided details as to the extent to which successive protonation alters the geometry and conformational characteristics of these species.

A more fundamental question to be addressed is the precise order of successive protonation of the basic atoms in these species. While in general nitrogen atoms are more basic than oxygen atoms and hence should protonate first, the proximity of the atoms involved gives rise to Coulombic effects which could alter the expected sequence. This has pertinence to the cis isomer in particular since the two nitrogen atoms lie on the same side of the molecular axis and therefore are closer to each other than they are in the trans isomer. The presence of significant Coulombic effects could result in a different sequence of protonation for the cis and trans isomers. Coulombic considerations also arise in considering the site of second protonation.

In the present study, geometry-optimized CNDO/2 (complete neglect of differential overlap) calculations were carried out to predict the order of protonation within the cis-PBO model compound. Also obtained are differences in proton binding energies between $N\text{-}H^+$ and $O\text{-}H^+$ in these species, as well as information regarding charge distributions and Coulombic effects. The results indicate that protonation occurs in the order nitrogen, nitrogen, oxygen, oxygen, which is consistent with the greater basicity of nitrogen relative to oxygen. Thus, repulsive Coulombic effects between the acidic protons have a negligible influence on the precise sequence of protonation. In fact, following initial protonation of a nitrogen atom, Coulombic energies alone favor protonation at the other nitrogen rather than at the more distant oxygen by ca. 0.7 kcal mol^{-1}. Both initial and second protonation is favored at the nitrogen rather than at the oxygen by ca. 60. kcal mol^{-1}, obtained by comparing the total CNDO/2 energies calculated for the resulting species.

Methodology

The technique employed consists of the CNDO/2 semi-empirical molecular orbital method (POPLE and BEVERIDGE, 1970) nested in an iterative scheme for achieving direct geometry optimization (KONDO, 1978). The initial geometry for the flat cis-PBO model compound was taken from a similar calculation on the unprotonated molecule (WELSH, et al., 1982) which in turn was nearly identical to that observed by X-ray analysis (WELLMAN, et al., 1979). The order of successive protonation was determined by comparing the geometry-optimized CNDO/2 total energy for the following different species: (1) one H^+ on a nitrogen atom, (2) one H^+ on an oxygen atom, (3) one H^+ on each nitrogen atom, (4) one H^+ on each oxygen atom, and (5) one H^+ on a nitrogen atom and another H^+ on an oxygen atom. In each case, the H^+ was initially placed in the same plane as the heterocyclic group at the typical bond distance (1.05 Å) away from the basic atom and bisecting the exo-ring angle. All calculations were applied to the model compound in the flat, coplanar form, which is the conformation observed in the crystalline state (WELLMAN, et al., 1979).

Results and Discussion

Comparison between the first two species mentioned above yields information regarding the initial site of protonation. The results indicate that the $N\text{-}H^+$ bond formation is preferred over that of $O\text{-}H^+$ by ca. 60.7 kcal mol^{-1}. Placing the acidic proton in a more tetrahedral arrangement relative to the oxygen atom (at various angles ranging from 30° to 60° out the plane of the heterocyclic ring) reduced the preference for protonation at N only to ca. 56 kcal mol^{-1}. This preference is qualitatively in agreement with, but quantitatively considerably larger than, values obtained by ab initio calculations on simple non-aromatic bases, such as H_2NOH and HNO which prefer protonation at N rather than at O by ca. 24.3 and 15.5 kcal mol^{-1}, respectively (DELBENE, 1982; DELBENE, et al., 1982). For these two species, the present methods yield preferences for N of ca. 33.0 and 14.2 kcal mol^{-1}, respectively. The agreement between the two methods is acceptable, suggesting that the value of 60.7 kcal mol^{-1} obtained in the present study may be realistic and not merely an artifact of the CNDO/2 technique itself.

A further indicator of the relative stability of the two bonds is obtained by comparison of the delocalization of the acidic proton's formal charge. Specifically, the proton retains a partial charge of 0.215e in the $N\text{-}H^+$ form compared with 0.330e in the $O\text{-}H^+$ form, demonstrating that the former case is superior in terms of charge delocalization. In terms of the alteration of the charge of the basic atom before and after it is protonated, however, there is little difference between the nitrogen and the oxygen. Specifically, the partial charge changes from $q = -0.301e$ to $q = -0.200e$ ($\Delta q = +0.10e$) for the nitrogen atom and from $q = -0.293e$ to $q = -0.205e$ ($\Delta q = +0.09e$) for the oxygen atom. Hence, an advantage in protonating at nitrogen rather than at oxygen lies more in its superiority in dispersing the proton's formal charge throughout the species and not primarily in the electron withdrawing ability of the basic atom per se. Calculated bond lengths are nearly the same, being 1.04 Å for $O\text{-}H^+$ and 1.06 Å for $N\text{-}H^+$.

Having established that initial protonation at one of the nitrogen atoms is preferred, comparison of the 3rd, 4th and 5th species considered provides information regarding the second site of protonation. The results indicate that protonation at the other nitrogen atom rather than at the more distant oxygen atom is preferred by ca. 63.6 kcal mol^{-1}, approximately the same value obtained for initial protonation. This preference is not immediately obvious since in this case the effects of possible Coulombic repulsions must be considered. Specifically, a second proton placed at the other nitrogen will be much closer (5.72 Å) to the initial proton than a second proton at the more distant oxygen atom (7.05 Å). This difference in proximity could result in more repulsive Coulombic interactions and hence a less preferred situation for the former case. However, comparisons of the two cases in this respect indicate that Coulombic energy differences are negligible relative to the differences in binding energies and actually *favor* second protonation at nitrogen. Application of Coulomb's Law $E_{coul} = \frac{q_1 q_2}{\varepsilon d_{12}}$ with $\varepsilon = 1$ yields $E_{coul} = 3.2$ kcal mol^{-1} and $E_{coul} = 3.9$ kcal mol^{-1} for the $H^+ \cdots H^+$ interaction energy for the case of N,N and N,O protonation, respectively. The slight Coulombic preference (less repulsion) for nitrogen protonation is a consequence of the protons having a smaller partial charge in this case, which offsets their closer proximity. Interestingly, in either case the second protonation again results in substantial delocalization of the proton's formal charge. Specifically, a second proton located at a nitrogen atom has $q = +0.237e$ while one at an oxygen atom has $q = +0.350e$. Both of these values are nearly identical to those occurring with initial protonation, so it appears that the middle benzene ring in the benzobisoxazole group acts as a charge buffer, thus preventing significant charge dispersal through it. In terms of the energetics and charge effects involved in protonation, each of the oxazole rings within a benzobisoxazole group appears to behave nearly independently of one another.

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