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Possible Anisotropy in Phenanthrene Overcrowding

Alec Grimison
Department of Chemistry, University of Puerto Rico

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Earlier work on the origin of the aplanarity of the phenanthrene molecule has been extended to determine the possible involvement of an anisotropic H–H potential in the distortion from planarity.

Key words: Phenanthrene, non-planarity of ~ – H–H repulsion, anisotropic, in phenanthrene

A recent paper [1] described a theoretical treatment of overcrowding in phenanthrene. An X-ray and neutron diffraction study [2] had confirmed a H(4)-H(5) distance of 2.04 Å, well below the Van der Waals distance of 2.4 Å, and that this close approach forces a slight distortion from planarity. The previous calculations were done using the complete neglect of differential overlap method [3] (CNDO/2). The two major questions studied in detail were the non-planarity, and the opening up of the C(12)-C(4)-H(4) bond angle to the experimental value of 121.6°.

The non-planarity, as explained in detail in [1], was studied by proportionately scaling a basic set of z-coordinates taken from the out-of-plane perpendicular distances given by the X-ray data [2]. A factor φ_z was used with values from $0.0-5.0$, where $\varphi_z = 1.0$ reproduces the out-of plane X-ray geometry and $\varphi_z = 0.0$ is the plane-projected X-ray geometry, both averaged to preserve C_2 symmetry. Separate CNDO calculations were made for each set of coordinates. For comparison, the results are repeated in Table 1 (second column) together with some interspersed values not previously calculated. It is clearly seen that the minimum energy configuration according to the CNDO calculations is the planar one. However, there are two possible interpretations of this result, as indicated earlier [1]. The first is that the minimum energy configuration of the isolated molecule is indeed the planar configuration, and that the small out-of-plane distortion is due to crystal forces. The second is that there is an anisotropic H–H repulsion [1, 2], whose effect might be obliterated by the averaging of integrals necessary to preserve rotational invariance in the CNDO method.

The CNDO results for the energy as a function of the C–C–H dihedral angle are also given in the second column of Table 2. The lowest energy calculated was for angles of 120–121°, in fair agreement with the experimental value of 121.6°, considering the shallowness of the minimum in the energy curve in this region. (Note the misprint in Table 7 of [1] where 121.5° should read 121.0°.)

Table 1. Effect of scaling out-of-plane distortions

Geometry	CNDO Energy (eV)	EHT Energy (eV)
X-ray vector, bond lengths [1]		
ρ_z = 0.0	-2913.535	-1164.650
0.5	-2913.534	-1164.650
1.0	-2913.532	-1164.662
2.0	-2913.520	-1164.672
2.5	-2913.511	-1164.675
3.0	-2913.499	-1164.679
3.5	-2913.484	-1164.674
4.0	-2913.467	-1164.672
4.5	-2913.445	-1164.663
5.5	-2913.386	-1164.657
6.0	-2913.348	-1164.646

Table 2. Energy as a function of the C–C–H dihedral angle

Geometry	CNDO Energy (eV)	EHT Energy (eV)
118.0°	-2913.520	-1164.626
119.0°	-2913.531	-1164.638
119.5°	-2913.534	-1164.642
120.0°	-2913.537	-1164.646
120.5°	-2913.538	-1164.650
121.0°	-2913.537	-1164.650
121.6°	-2913.535	-1164.650
122.0°	-2913.533	-1164.648
124.0°	-2913.507	-1164.627
126.0°	-2913.461	-1164.590

In view of the conclusion [1] that the CNDO method is probably not the most appropriate for studing possible anisotropic interactions, the above calculations have been repeated using the extended Hückel theory method [4] (EHT). The results are presented in the third columns of Table 1 and 2. The immediate observation from Table 1 is that the EHT calculations in fact predict a minimum energy configuration with a deviation from planarity, the minimum ocurring at around three times the experimental distortion. Thus the EHT calculations suggest an aplanar isolated molecule, and therefore that the experimentally observed distortion is not due to crystal forces. As explained earlier [1], the increase in H–H distance produced by such a small distortion is very slight, so that the H–H potential may indeed be strongly anisotropic. The failure of the CNDO method to demonstrate this effect is extremely interesting. The actual quantitative results seem in reasonable agreement with experiments in view of the extremely small magnitude of the distortion ($\sim 1°$ in each direction).

The results of Table 2 show a very close similarity between the CNDO and EHT results, even to the numerical changes in energy for a particular change in dihedral angle. It is important to note that the total energies being compared are the electronic plus nuclear CNDO energies and the electronic EHT energies. This procedure is inevitable but not rigorously defensible. (The EHT method discards both nuclear energies and electronic repulsion energies, but produces "energies" in apparent accord with experiment.) The EHT can be seen to give a shallow energy minimum in the range 120.5–121.6°.

In conclusion, in this particular instance, the EHT method [4] has been shown to give a much better account of the phenanthrene aplanarity than the CNDO method [3]. The results for the opening up of the C–C–H dihedral angle in the overcrowded region are identical. It indeed appears that the H(4)-H(5) repulsion may be strongly anisotropic. Such effects apparently *can* be obscured by the averaging of integrals to preserve rotational invariance in the CNDO method. CNDO calculations are thus not particularly appropriate for nearly planar systems, where there is little arbitrariness in the choice of coordinate axes, so that the preservation of rotational invariance is not an important consideration.

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Prof. Alec Grimison
Chemistry Department
University of Puerto Rico
Rio Piedras, Puerto Rico 00931