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Ground States of Molecules

XXIII.* MINDO/2 Calculations for Naphthalene**

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Detailed MINDO/2 calculations of naphthalene using the SIMPLEX minimization algorithm are reported. Comparison of results with experiment and various π approximations is made.The results are in good agreement with experiment.

The geometry of naphthalene has been of considerable interest to theoreticians both because it has been determined with unusual precision by X-ray crystallography [1] and electron diffraction [2] and because the majority of theoretical treatments have failed to account for the length of the 9, 10 bond. We have now studied this problem in detail, using MINDO/2 [3].

Recent work in these laboratories has led to the development of a semiempirical SCF MO procedure (MINDO/2 [3]) which seems to give good estimates of ground state properties. We have also developed a procedure [4], based on the SIMPLEX algorithm [5] for calculating molecular geometries. Application of these techniques to naphthalene seemed of interest for two reasons. First, we have recently modified [6] the parameters in MINDO/2 to overcome two of its shortcomings, i. e. the systematic overestimation of dipole moments (by ca. 50%) and of lengths of bonds involving hydrogen (by 0.1 Å); calculations for naphthalene seemed to provide a good test of its ability to still deal adequately with CC bonds. And secondly, such a calculation seemed to provide a good test of our SIMPLEX program in a molecule whose geometry involves a rather large number of independent coordinates.

Since the number of coordinates was so large, the calculation was carried out in stages. We first assumed all the CH bonds to have the same length (1.09 Å) and to bisect the adjacent CCC bond angle; the CC bond lengths and CCC bond angles were calculated on this basis by a standard SIMPLEX minimization. Assuming these CC bond lengths and CC bond angles, we then calculated the CH bond lengths and HCC bond angles by a second SIMPLEX minimization. As a check, the cycle was repeated; the bond lengths, bond angles, and energy from the second cycle were identical within the limits of accuracy of the SCF treatment, with those from the first. Since the number of SCF calculations for SIMPLEX minimization of a system with n independent coordinates is approximately n^2, this type of iterative procedure should prove helpful for large molecules since it evidently can converge quite rapidly.

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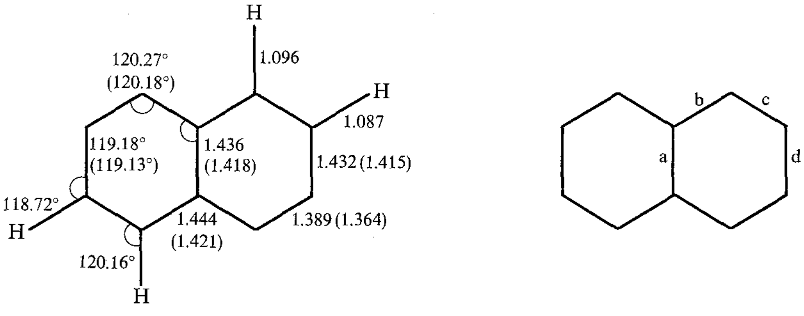

(a) (b)

Fig. 1. (a) Calculated (observed [1]) bond lengths (Å) and bond angles in naphthalene; (b) key to Table 1

The final geometry is indicated in Fig. 1, together with Cruickshank's experimental values [1]. The calculated heat of formation (18.6 kcal/mole) was less than that observed (36.2 kcal/mole).

The agreement between the calculated and observed bond angles is almost perfect. The calculated CC bond lengths are systematically too long; if a corre-

Table 1. Bond lengths for naphthalene, calculated by various methods and observed

Method[a]	*a*[b]	*b*[b]	*c*[b]	*d*[b]	*Ref.*
This paper	1.436	1.444	1.389	1.432	
SCF-π	1.420	1.426	1.382	1.419	[c]
SC-π	1.396	1.424	1.364	1.418	[d]
SCF-CI	1.415	1.423	1.380	1.416	[e]
MO-SC	1.419	1.420	1.382	1.414	[f]
HMO	1.409	1.439	1.363	1.432	[g]
SCP	1.412	1.425	1.378	1.418	[h]
PEO	1.408	1.424	1.369	1.417	[i]
VB	1.407	1.434	1.377	1.428	[j]
SMO	1.424	1.416	1.384	1.406	[k]
X-ray	1.418	1.421	1.364	1.415	[l]
ED	1.420	1.422	1.371	1.412	[m]

[a] SCF-π, semiempirical SCF MO π approximation with parameters chosen to reproduce ground state properties; SCF-CI, Pople π approximation with configuration interaction; MO-SC, self-consistent HMO; HMO, refined Hückel MO; SCF, self-consistent perturbation theory; PED, projected electron density; VB, valence bond; ED, electron diffration.

[b] For key, see Fig. 1(b).

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sponding correction (0.021 Å) is made, the errors are then all less than ± 0.005 Å, within the limits of error of the X-ray crystallographic analysis [1]. The calculated CH bond lengths agree with the electron diffraction [2] value (1.09 Å).

Table 1 compares bond lengths for naphthalene calculated by various π approximations with the values in Fig. 1 and with experiment. It will be seen that MINDO/2 reproduces the relative lengths more accurately than any of the π approximations, suggesting that reasonable reliance can be placed in its predictions for molecules even as large as this.

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