Tetrahedron Letters,Vol.24,No.28,pp 2893-2896,1983 0040-4039/83 $3.00 + .00
Printed in Great Britain

A SINGLE MOLECULE AND CRYSTAL STATE CONFORMATION OF 9,10-DIHYDROANTHRACENE. A THEORETICAL STUDY

A. Sygula and T.A. Holak
Institute of Chemistry, Jagiellonian University
30-060 Krakow, Poland

Results from MNDO and QCFF/PI+MCA calculations predict the boat-shaped conformation of 9,10-dihydroanthracene to be of lowest potential energy in both the gaseous phase and the solid state. Entropy contribution favors further the boat-shaped conformation over the planar form.

The conformational analysis of the 1,4-cyclohexadiene ring system has been the subject of a substantial number of theoretical and experimental investigations.[1-3] The conformational preference of the parent 1,4-cyclohexadiene 1 and 1,4-dihydronaphthalene 2 (planar vs. boat/equilibrating boats) has caused considerable controversy although by 1981 these difficulties appeared to be resolved and the most stable conformation for 1 and 2 were established to be planar.[1,2] On the other hand 9,10-dihydroanthracene 3 has been shown by X-ray diffraction to be nonplanar in the solid state[4] and is presumed to undergo rapid boat to boat ring inversion on the NMR time scale at least at -60 °C.[5]

We have carried out theoretical calculations of crystal and single molecule geometries of 3 with the QCFF/PI+MCA[6] and MNDO[7] methods in order to clarify the relationship existing between the preferred conformations of 3 in the two states of matter. For comparison, the structures of 1 and 2 were also calculated with the MNDO method. The calculations were performed with optimization of all independent bond lengths and bond angles for the C_{2v} (nonplanar structures) and D_{2h} (in the case of planar structures) symmetry restrictions.

Recently a careful computational study of 1-3 has been published.[2a] Using molecular mechanics, MMI, it has been shown by calculations that the optimum structure is planar for each molecule although the energy required for nonplanar distortion is small and decreases regularly with the degree of benzannulation. A thorough investigation of 1 by means of MM2 and molecular orbital methods, MINDO/3, MNDO, and ab initio, gave qualitatively the same results.[2] A note added in proof cited the limited results of MM2 and MNDO calculations for 3.[2a] Both methods afforded an optimum geometry which is nonplanar, while the MINDO/3 method predicts the planar conformation to be preferred. It was concluded that the nonplanar X-ray structure may not represent the preferred geometry of 3 in solution or in the gas phase.

Our MNDO results for 1 are identical with those of the calculations cited above. For 2 we calculated the planar conformation to be the most stable and more stable than the 160° boat conformation by ca 0.4 kcal/mol, see Figure 1. The MNDO energy profile for 3 is also given in Figure 1 and the full details of the MNDO results are collected in Table I. As can be seen from Figure 1, MNDO predicts the boat-shaped conformation with $\phi=159^{\circ}$ to be the most stable for 3 in contrast to the planar forms of 1 and 2. It is known that MNDO flattens optimal structures of nonplanar cyclic compounds relative to the experimental geometries.[7] Thus the MNDO prediction that the nonplanar form is the most stable form for 3 in the gas phase does not appear to be an artifact. The X-ray structure for 3, with $\phi=145^{\circ}$, would support this conclusion if one can assume that crystal packing forces do not perturb appreciably the structure of 3 in the solid state. However, the extremely flat energy surface for 3 does not allow for such an assumption to be a priori admissible. The results of the QCFF/PI+MCA calculations should show whether the nonplanarity of 3 is its intrinsic property both in the gas and crystal state. The preferred QCFF/PI conformation of 3 in the gas phase is boat-shaped with $\phi=135.2^{\circ}$, Table I. This is in a qualitative agreement with the MNDO results although QCFF predicts the ring of 3 to be significantly more puckered.

The optimal conformation of 3 in the crystal[8] was also calculated to be boat-shaped with $\phi=138.5^{\circ}$. This shows that crystal packing forces do not affect significantly the preferred conformation of 3. Moreover, the results of the QCFF calculations indicate that 3 is slightly flattened in the crystal, as compared with the isolated molecule. This strongly supports the conclusion that the boat-shaped structure of 3 is also preferred in the gas phase.

The right location of the molecule in the unit cell is confirmed by comparison of the computed and experimental (in parenthesis) angles which are made by vectors $\overline{OA}$, $\overline{OB}$, and $\overline{OC}$, see Figure 1, with the Cartesian coordinate axes x, y, and z, respectively. The angles for $\overline{OA}$ are 49.2° (52.5°), 102.3° (105.0°), and 137.2° (138.5°); for $\overline{OB}$ 92.6° (96.0°), 93.0° (93.0°), and 4.0° (7.0°); for $\overline{OC}$ 64.4° (63.0°), 25.5° (27.5°), and 86.1° (85.0°). Equilibrium Cartesian coordinates calculated by QCFF/PI+MCA for 3 are given in Table II since results of detailed X-ray crystal structure analysis are not presently available in the literature. The energy of 3 in the crystal, corrected for difference in the vibrational enthalpies at room temperature, is 25.05 kcal/mol lower than that for the gas phase, in reasonable agreement with the measured sublimation energy of 3, 22.52 kcal/mol at 298 °K.[9]

In conclusion our comparative molecular mechanics and molecular orbital calculations show that the boat-shaped conformation of 3 is the most stable both in the gas and crystal state, although variation of the potential energy is small for ϕ in the range 140°-180°. From MNDO the potential energy difference between the most stable boat-shaped form and the planar form is ca. 40 cal/mol. Additionaly however, entropy contribution should favor further the boat-shaped form versus the planar one by ca. 2.8 e.u. (contribution of a symmetry number term to the entropy difference $S_{boat}-S_{planar}$ equals to +1.38 e.u. and since there are two conformational isomers for the boat form and one for the planar form, the contribution from the "mixing" term is Rln2=+1.38 e.u.). 9,10-Dihydroanthracene has thus the boat-shaped structure with a small activation barrier for the ring inversion leading to rapid inversion of one boat-shaped form to another.

Table I. Structural parameters for the isolated molecule of 9,10-dihydroanthracene, 3

Bond length, Å	MNDO	QCFF/PI	Bond angles, deg	MNDO	QCFF/PI
C1 - C2	1.402	1.406	C1 - C2 - C3	119.9	120.1
C2 - C3	1.406	1.404	C9a- C1 - C2	120.9	120.2
C9a- C10a	1.419	1.422	C1 - C9a- C10a	119.2	119.6
C9a- C1	1.416	1.408	C9a- C9 - C9b	115.1	108.1
C9a- C9	1.512	1.495	C9 - C9a- C10a	120.8	119.6
C1 - H1	1.092	1.083	H1 - C1 - C9a	119.9	120.4
C2 - H2	1.091	1.083	H2 - C2 - C3	120.1	120.0
C9 - H9	1.116	1.111	H9 - C9 - C9a	108.8	110.7
C9 - H9′	1.118	1.112	H9′- C9 - C9a	108.8	110.2
			ϕ	159.0	135.2

Table II. Equilibrium Cartesian coordinates of 3 in the crystal calculated by QCFF/PI+MCA, Å

	x	y	z		x	y	z
C1	1.981	0.584	1.150	C10a	-0.590	-0.775	4.137
C2	2.458	-0.352	0.217	H1	2.440	1.563	1.202
C3	1.869	-1.623	0.130	H2	3.280	-0.091	-0.437
C4	0.794	-1.960	0.970	H3	2.239	-2.344	-0.587
C5	-0.921	-1.479	5.310	H4	0.347	-2.941	0.888
C6	-0.698	-0.897	6.569	H5	-1.365	-2.464	5.250
C7	-0.119	0.379	6.664	H6	-0.976	-1.437	7.465
C8	0.250	1.076	5.501	H7	0.047	0.827	7.635
C9	0.372	1.242	2.984	H8	0.701	2.056	5.588
C10	-0.852	-1.365	2.790	H9a	1.112	2.042	3.191
C9a	0.909	0.254	2.001	H9b	-0.536	1.728	2.567
C9b	0.020	0.506	4.234	H10a	-0.990	-2.461	2.862
C10a	0.296	-1.025	1.896	H10b	-1.796	-0.950	2.379

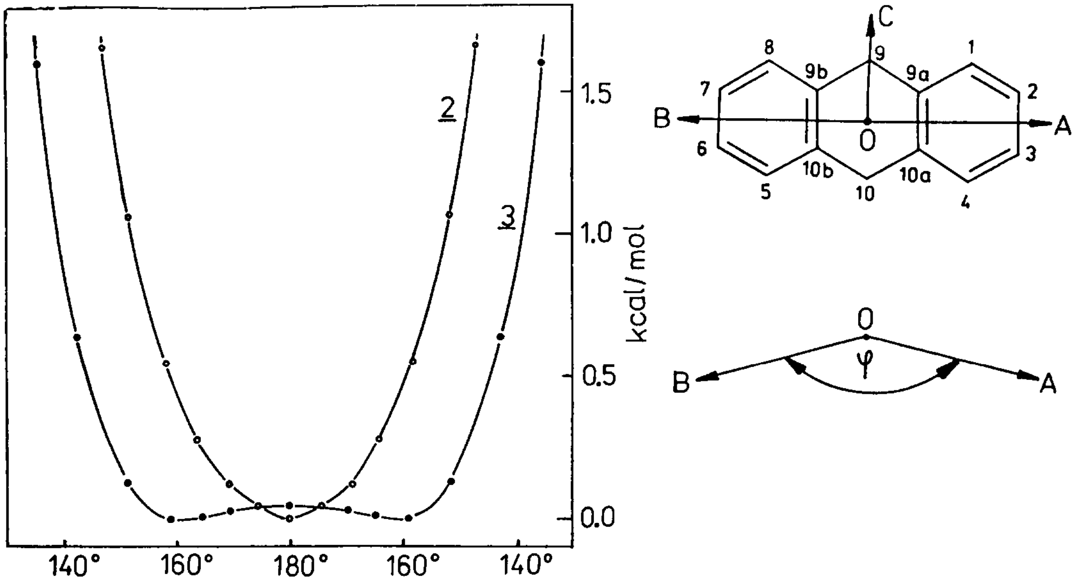

Figure 1. Potential energy curves for 2 and 3 as functions of the angle ϕ.

REFERENCES AND NOTES

1. For a critical review see P. W. Rabideau, Acc. Chem. Res. 1978, 11, 141.
2. (a) K. B. Lipkowitz, P. W. Rabideau, D. J. Raber, L. E. Hardee, P. v. R. Schleyer, A. J. Kos, and R. A. Kahn, J. Org. Chem. 1982, 47, 1002; (b) D. J. Raber, L. E. Hardee, P. W. Rabideau, and K. B. Lipkowitz, J. Am. Chem. Soc. 1982, 104, 2843; (c) A. J. Birch, A. L. Hinde, and L. Radom, J. Am. Chem. Soc. 1981, 103, 284; (d) S. Saebo and J. E. Boggs, J. Mol. Struct. 1981, 73, 137.
3. D. K. Dalling, K. W. Zilm, D. M. Grant, W. A. Heeschen, W. J. Horton, and R. J. Pugmire, J. Am. Chem. Soc. 1981, 103, 4817.
4. W. G. Ferrier and J. Iball, Chem. Ind. 1954, 1296.
5. W. B. Smith and B. A. Shoulders, J. Phys. Chem. 1965, 69, 2022.
6. A. Warshel and M. Levitt, 1974, QCPE 247, Quantum Chem. Programs Exchange, Indiana Univ., E. Huler, R. Sharon, and A. Warshel, 1976, QCPE 325.
7. M. J. S. Dewar and W. Thiel, J. Am. Chem. Soc. 1977, 99, 4893, 4907.
8. Crystal structure calculations for 3 were performed using as input data unit cell parameters: a=7.70 Å, b=6.21 Å, c=11.09 Å, $\alpha=\gamma=90^{\circ}$, $\beta=113.0^{\circ}$, and the space group ($P2_1$, Z=2) given by Ferrier and Iball.[4] 46 Molecules of 3 for which the minimal atom-atom distance to the central molecule does not exceed 7 Å were taken into the calculations. The total energy was minimized with respect to 78 Cartesian coordinates of the central atoms.
9. L. Malaspina, R. Gigli, G. Bardi, and G. DeMaria, Conf. Int. Thermodyn. Chim. C. R., 4th, 1975, 1, 54 ; CA. 1976, 84: 179387v.

(Received in UK 3 May 1983)