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THE PREFERRED CONFORMATION OF 3-PHENYLSYDNONE, AN E.H.T.-M.O. CALCULATION

by

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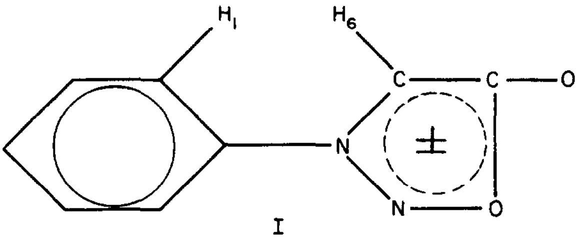
Early Hückel M.O. calculations of the electronic structure of the sydnones(1, 2) did not produce results mirroring physical experience. More recently Bochvar and Bogaturyants(3) reported some correlation of bond length with simple Hückel M.O. bond orders. Kier and Roche,(4) using the ω-Hückel technique with suitably derived parameters, have calculated correct dipole moments and have found a correlation of calculated energies with electronic spectra. The method treated the σ and the π electrons separately. The σ skeleton was calculated with a LCBO-MO method.(5) The recent introduction of the extended Hückel method by Hoffmann(6) affords a procedure whereby both σ and π electrons in complex molecules may be treated at the same time and without the need for separate parameterization. Because the extended Hückel procedure includes in the input, precise 3-dimensional coordinates of the atoms, the method is sensitive to assigned conformation. Indeed one of the successes of the method is the ability to correctly predict the preferred conformation of numerous molecules.(7, 8)

Previous reports using the E.H.T. method to predict conformation have been confined exclusively to hydrocarbons. No successful efforts have been reported involving molecules containing heteroatoms. Indeed, the method has experienced difficulties with heteroatoms, as for example the prediction of a linear water molecule.(9) In the light of these problems, it is truly remarkable that these calculations on phenylsydnone, involving two different heteroatoms, each in a different valence state, will produce the correct experimental conformation.

In this study, we have calculated the total energy of 3-phenylsydnone, I, at several inter-ring dihedral angles. The parameters used were those commonly employed.(9, 10) The bond angles were taken from Bärmighausen's X-ray study,(11) in which a dihedral angle of 27.6° between the rings was found.



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The calculated total energies for several dihedral angles are listed in Table 1 and plotted against the angle in Figure 1. The calculations result in an energy minimum corresponding to 27°, in excellent agreement with the 27.6° angle from X-ray measurement.(11) The angle is a result of two principal effects, the repulsion of two hydrogens (phenyl ortho H_1 and the sydnone H_6) and the increased conjugation due to π overlap in a planar conformation. The two effects are opposed and the resultant produces a minimum in the potential energy curve. As can be seen from Figure 1, the repulsive effects of the two hydrogens appear to be the predominant factor in determining the dihedral angle. The H_1-H_6 distance is close to the value of 2 hydrogen van der Waals radii, hence little interpenetration of their radii exists even though it would produce a lower potential energy by increasing the π overlap between the two rings.

The barrier to rotation is calculated to be 2.76 kcal, a value well within the usual reported values for single bond rotation barriers, where only hydrogens are eclipsed.

The calculated charge densities are shown in Figure 2. The values are high in an absolute sense, a common occurrence with the E.H.T. method. The calculated dipole moment from these charge densities is 12.5 D, about twice the experimental value of 6.48 D reported.(12) Nevertheless, the π charge density values are of the same sign and relative magnitude as those previously reported.(4)

TABLE 1. CALCULATED ENERGIES, H_1-H_6 DISTANCES AND OVERLAPS

θ°	E (kcal)	R (Å)	Overlap H_1-H_6
0	-26,639.05	2.08	0.197
20	40.45	2.21	0.169
27	41.81	2.30	0.150
30	41.80	2.36	0.141
40	40.52	2.54	0.111
50	40.55	2.74	0.085
90	39.60	3.64	0.024

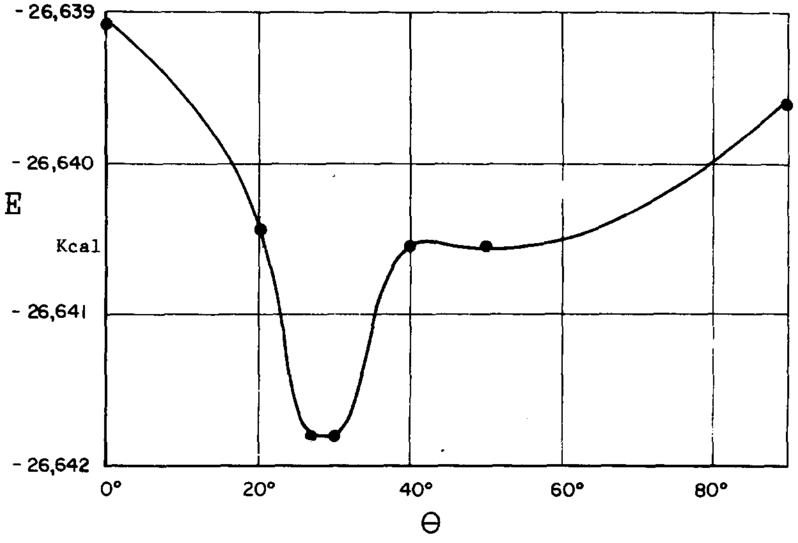

FIGURE 1. CALCULATED TOTAL ENERGIES VS. DIHEDRAL ANGLE

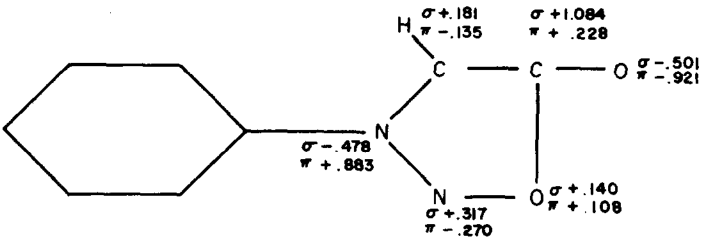

FIGURE 2. CALCULATED CHARGE DENSITIES FOR 3-PHENYLSYDNONE

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