Tetrahedron. Vol. 27, pp. 6151–6158. Pergamon Press 1971. Printed in Great Britain

THE CONFORMATION OF DIPHENYL ETHER, SULPHIDE AND SELENIDE

A QUANTUM-MECHANICAL INTERPRETATION

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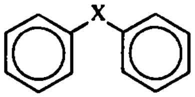
(*Received in the UK* 1971; *Accepted for publication* 3 *August* 1971)

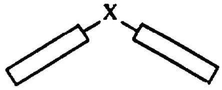
Abstract—An attempt has been made to explain the conformation of the title compounds by investigating the potential energy surfaces with the aid of the EH–MO theory. The "butterfly" structure D is found to be energetically most favoured. On the other hand, the small energy barriers predicted between the principal conformations B, C, and D support the hypothesis of a non-rigid structure for these compounds. In connection with this viewpoint discussion is given on possible pathways of interconversion from the preferred geometry to its enantiomer.

The present calculations also show that inclusion of 3d orbitals on sulphur causes no change in the geometry and only a small effect on the rotational barriers for diphenyl sulphide.

INSPECTION of the literature reveals that discrepant conclusions on the stereochemistry of diphenyl ether, sulphide, and selenide (Ph_2X where X = O, S, and Se) have been drawn from the available experimental evidence.[1–4] Four distinct types of *rigid* conformations have been considered, *viz*. A, B, C, and D:



A



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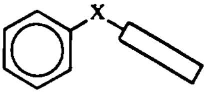

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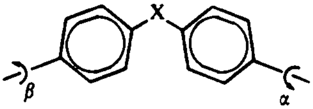

D

A is the all-planar structure.[5] In B the Ph ring planes are perpendicular to the C–X–C plane.[6] In the "skewed" form C, referred to as the "Morino structure",[7] the Ph ring planes are orthogonal. Finally, in the "butterfly" conformation D[8] the Ph groups are rotated about their C–X bonds by angles α and β out of coplanarity with the C–X–C triangle. Clearly, form A is made impossible by one short H–H contact, and the minimal conjugation of oxygen with the Ph rings counterindicates form B. On the other hand, structure C and/or structure D have been invoked by many authors to account for various experimental data.[1–4] The hypothesis of *non-rigid* structure, in which both benzene rings can rotate in the manner of cog-wheels, has been advanced by

Higasi[4] on the basis of dielectric relaxation measurements and quite recently has been proved by Garrigou-Lagrange *et al.*[3] to be in accordance with the vibrational and NMR spectra of diphenyl ethers.

Do these molecules adopt any definite equilibrium conformation, as determined by a delicate balance of steric and conjugative factors or, do they behave as nearly free rotors? It is clear that a conclusive answer to this conformational problem requires further experimental information. However, theoretical investigations may also prove useful. An extensive exploration of the potential energy surfaces, including all possible simultaneous rotations of the two Ph groups in these molecules, is the object of the present paper.

In dealing with the problem of the geometry of large-size molecules, non-empirical calculations are, with present technology, completely out of question. On the other hand, calculations with all-valence-electron semiempirical methods like CNDO[9] or (M)INDO[10, 11] and even with the iterative Extended Hückel (EH) method[12] are still lengthy and expensive. However, during the last few years the standard EH theory[13] has been applied with a reasonable degree of success in the prediction of the most stable conformation of a number of organic and inorganic molecules as well as of biopolymers. For these reasons use has been made here of the EH-MO pragmatic approach to investigate the relative stabilities of all the possible conformations of the three molecules Ph_2X and the nature of the rotational barriers around their Ph-X linkages. The procedure enables us to pick out the preferred conformations and to study the mechanisms of interconversion.

COMPUTATIONAL DETAILS

The calculations have been performed by means of the semi-empirical EH method,[13] in which all valence electrons are explicitly treated and all overlap integrals are included. Slater-type orbitals used as the basis set have been 1s of H, 2s and 2p of C and O, 3s and 3p of S, and 4s and 4p of Se: a total of 62 orbitals per molecule. The values of the valence state ionization potentials (VSIP's) are listed in Table 1 together with the orbital exponents. The values of the exponents are those given by Clementi and Raimondi[14] except the one for H, where 1·3[15] has been preferred to the usual 1·0 value.

TABLE 1. PARAMETERS OF THE EH CALCULATIONS

Atom	Orbital	Exponent	VSIP (ev)
H	1s	1·3000 [15]	13·6 [16]
C	2s	1·6083 [14]	21·4 [16]
	2p	1·5679 [14]	11·4 [16]
O	2s	2·2458 [14]	32·3 [16]
	2p	2·2266 [14]	14·8 [16]
S	3s	2·1223 [14]	20·1 [17]
	3p	1·8273 [14]	13·3 [17]
Se	4s	2·4394 [14]	20·5 [18]
	4p	2·0718 [14]	14·5 [18]

Since structural determinations for the unsubstituted molecules Ph_2X are lacking, the C–X distances and the C–X–C angles have been taken from their *p*-derivatives and the other geometrical parameters have been given standard values: C–C 1·39Å, C–H 1·08 Å, C–O 1·40 Å,[19] C–S 1·75 Å,[20,21] C–Se 1·92 Å,[22] angle C–O–C 123°,[19] angle C–S–C 109·5°,[20] angle C–Se–C 106°,[22] other angles 120°.

All possible conformations generated by rotation of both the Ph rings around their respective Ph–X axes as shown in the conventional structure D have been considered. In particular, a grid of points of 15° increments of the twist angles α and β has been scrutinized but a width as small as 3° has been used for studying the energy contours in the *minimum* regions. In all, some 50 points per molecule have been considered.

The program written by the authors has been run on an IBM 7044 at the "Centro di Calcolo" of Trieste University. Input to the program consists of orbital exponents, VSIP's, bond lengths and angles; a routine enables all geometries of a molecule to be run with only one loading of geometrical parameters. The output includes one-electron energy levels, total orbital energy, and Mulliken population analysis. The computation time is roughly 2′ 30″ per point on the potential energy surface.

RESULTS AND DISCUSSION

In Figs 1–3 the results for the ground-state of the three molecules Ph_2X are plotted as contour maps of the energy relative to an energy zero at the most stable conformation. In these diagrams the axes measure the angles of twist of the phenyl groups away from coplanarity. Only the intervals $-90° \leqslant \alpha \leqslant +90°$, $0° \leqslant \beta \leqslant 180°$ are

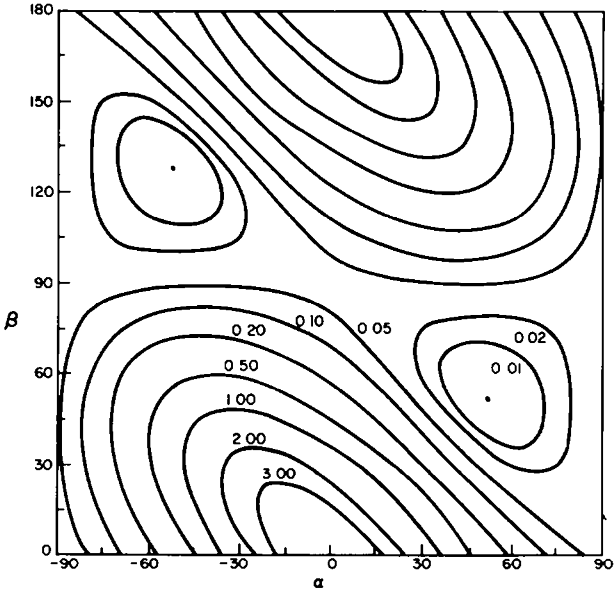

FIG. 1. Potential energy surface of diphenyl ether. The signs of α and β are defined relative to the sense of rotation shown in structure D. α and β are equal to zero for the planar conformation. The energy contours are in electron volts relative to the marked minima.

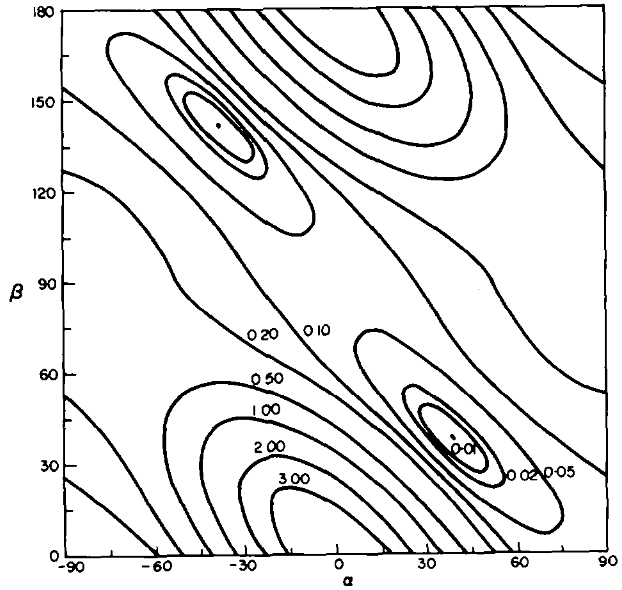

FIG 2. Potential energy surface of diphenyl sulphide. See caption to Fig. 1 for other details.

included in the plots since all the other geometries are identical by symmetry with those represented. The figures are generated by juxtaposition of only two symmetry non-equivalent triangular sections: a conrotatory region ($0^\circ \leqslant \alpha \leqslant 90^\circ$. $0^\circ \leqslant \beta \leqslant \alpha$), and a disrotatory region ($-90^\circ \leqslant \alpha \leqslant 0^\circ$, $0^\circ \leqslant \beta \leqslant |\alpha|$).

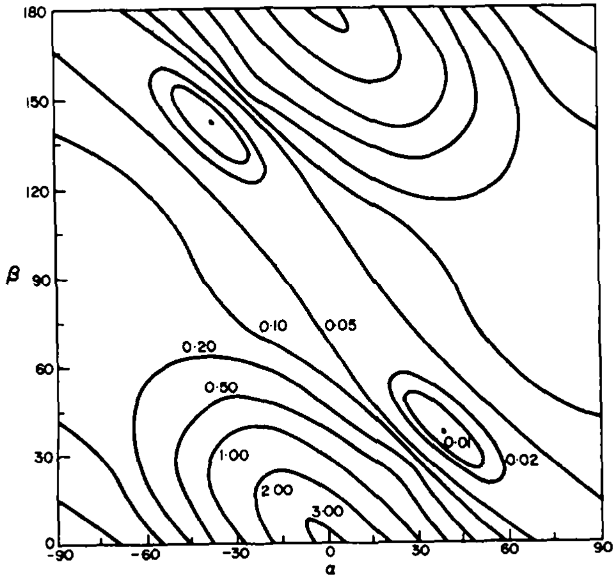

FIG 3. Potential energy surface of diphenyl selenide. See caption to Fig. 1 for other details.

For each molecule the disrotatory region clearly appears to be consistently of higher energy than the conrotatory. As expected the all-planar geometry (structure A) lies in a sterically forbidden region. It represents an energy maximum and is the least likely conformation. In addition the contour diagrams clearly show that there are no minima in the disrotatory region. The energetically most favoured geometry is found to be one along the line $\alpha = \beta$ within the conrotatory region. In particular, a shallow minimum occurs at $\alpha = \beta = 52°$ (and its mirror image at $\alpha = -52°$, $\beta = 128°$) for Ph_2O, and at $\alpha = \beta = 38°$ (and its mirror image at $\alpha = -38°$, $\beta = 142°$) both for Ph_2S and Ph_2Se. Although these points do not represent very deep energy minima, they do indicate minima in the twist angles α and β. Thus according to the calculations the relief of steric hindrance between the *ortho* H atoms and the decrease in resonance energy resulting from non-planarity are practically balanced in a butterfly conformation D.* Therefore these results indicate that if the structure of the Ph_2X molecules is rigid or quasi-rigid then at the equilibrium it must be of type D.

At this point an inspection of the experimental results compatible with an equilibrium structure of type D is in order.

Diphenyl ether. The molar Kerr constant derived from experiment in benzene solution has been interpreted in terms of conformation D with $\alpha = \beta = 37°$: this value of angle of twist is however given as an order of magnitude only.[8] A twist angle of about 50° has been proposed by Nagakura[4] from UV spectra analysis. Katayama's X-ray diffraction study[4] is consistent with an angle of twist of 17·5°.

Diphenyl sulphide. The molar Kerr constant measured in benzene solution is in reasonable agreement with structure D for which $\alpha = \beta = 42°$ [23] or 46°.[2] X-ray results[21] indicate that in the solid state di-*p*-tolyl sulphide has a configuration similar to D with twist angles of *ca.* 35°.

Diphenyl selenide. The molar Kerr constant reported for benzene solution is satisfactorily reconcilable with model D with $\alpha = \beta = 48°$.[2] In crystalline di-*p*-tolyl selenide each ring is twisted *ca.* 35° about the C–Se bond out the C–Se–C plane.[22]

Discrepancies sometimes striking between the conclusions derived from experiments are so far evident. However it is worthwhile to note the good consistency of the present theoretical predictions with UV evidence in the case of Ph_2O and with X-ray informations both for Ph_2S and Ph_2Se.

An aspect of the present results, which is perhaps still more significant than the theoretical predictions on the most probable conformations is that the energy differences between the most stable conformations and the structures B and C are only of the order of a few Kcal/mole or even less. The problem one is then faced with involves studying the possible pathways of interconversion of the preferred conformation into its enantiomeric form. For the present molecules Ph_2X the same three geared motion considered by Hoffmann and Swenson[15] for benzophenone and diagramatically schematized below can be properly taken into account:

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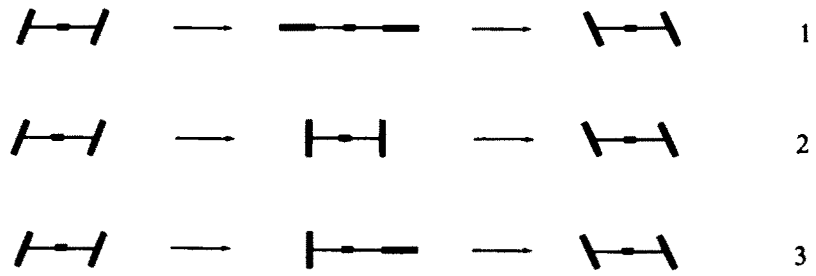
* Another mechanism for relief of steric hindrance is the enlargement of the valency angle C–X–C. In order to take into account this factor the construction, still time-consuming and expensive, of an energy hypersurface should be performed. It must be recalled, however, that since the C–X bonds are virtually single bonds the twist around them takes place more easily than the bending of the valency angle C–X–C. For these reasons the molecule Ph_2X has been assumed to have freedom of internal rotation but constant valency angle C–X–C.



The transition state bears the form A in mechanism 1, the skewed form B in mechanism 2 and the Morino structure in mechanism 3. respectively. Inspection of Figs 1–3 distinctly reveals that in all cases the transition state for motion 1 is the worst. Mechanism 2 is the most favourable in the case of Ph_2O. Instead, Ph_2S and Ph_2Se show clear preference for mechanism 3. The calculated barrier height in Ph_2O is 0·64 Kcal/mole for the geared motion 2. On the other hand. the theoretical activation energy for mechanism 3 amounts to 1·27 Kcal/mole for Ph_2S and to 0·90 Kcal/mole for Ph_2Se. Moreover mechanism 2 is only slightly favoured (0·3 Kcal/mole) over mechanism 3 in the case of Ph_2O. while mechanism 3 is clearly preferred to mechanism 2 in the case of Ph_2S (5·5 Kcal/mole) and Ph_2Se (3·4 Kcal/mole).

Although the EH-theory usually fails to account quantitatively for the barrier heights.[13] the authors believe that a trustworthy information can be obtained from the present results: *The considerably small potential energy barriers predicted for the molecules Ph_2X allow for continuous rapid interconversion of the most stable form into its enantiomer.* So far, the present results substantiate quantitatively the hypothesis of non-rigid structure invoked by some authors[3,4] to explain various experimental observations. In connection with this viewpoint it is of interest to note that for Ph_2O Castellano *et al.*[24] give only one chemical shift for all the *ortho* and another one for all the *meta* protons, and similarly Lardon[25] gives the same chemical shift for all the *ortho* protons of Ph_2Se. This could be an evidence that. at room temperature, there is rapid (NMR time scale) rotation of the Ph rings about the C–X linkages. while the alternative explanation, *i.e.* the existence of a rigid structure of type B, does not seem plausible on energetic grounds.

The present treatment yielded also the ground-state gross charge distribution of the Ph_2X molecules. The net atomic charges given by Mulliken's population analysis for the most probable conformation of each molecule are reported in Table 2. About these values it is pertinent to notice that the EH-theory has a largely-experienced tendency to over-emphasize the charge separation in heteroatomic systems.

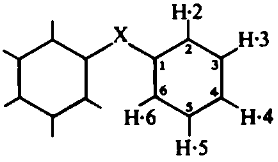
On the role of 3d orbitals in diphenyl sulphide

The importance of d-orbital participation in aryl sulphides is a much debated question.[26–31] Thus. in order to assess quantitatively if the inclusion of sulphur d-orbitals in the basis set affects the ground-state conformation of diphenyl sulphide, an EH calculation was carried out on diphenyl sulphide including the latter orbitals. The 3d sulphur orbitals, not given by Clementi and Raimondi,[14] were taken as Slater-type orbitals with exponent equal to 1·2[32] and with VSIP of 2 ev.[33]

TABLE 2. NET ATOMIC CHARGES*

Atom	Ph_2O	Ph_2S	Ph_2Se
X	-0·802	-0·044	-0·265
C-1	+0·530	+0·181	+0·232
C-2	-0·082	-0·082	-0·061
C-3	-0·017	-0·022	-0·022
C-4	-0·061	-0·072	-0·055
C-5	-0·017	-0·022	-0·021
C-6	-0·081	-0·079	-0·059
H-2	+0·029	+0·023	+0·023
H-3	+0·024	+0·024	+0·024
H-4	+0·023	+0·023	+0·023
H-5	+0·024	+0·024	+0·024
H-6	+0·029	+0·024	+0·024

* Atom numbering is assumed to be as follows:



The most probable conformation is predicted to be of type D with twist angles $\alpha = \beta = 38°$, which is the same geometry found with the restricted basis sp. As regards the rotational barriers for the interconversion of the preferred conformations, these are estimated to be slightly lower than in the case of the basis sp.

Thus, according to the results presented here the inclusion of d-orbitals, energetically unfavourable and diffuse, in the basis set does not modify the quantum-chemical interpretation of the conformation of diphenyl sulphide as provided by considering the sp interaction alone. In other words, the role of d-orbital participation if operating, seems to be unimportant in the ground-state of diphenyl sulphide.

CONCLUSIONS

A quantum-mechanical interpretation of the ground-state conformation of diphenyl ether, sulphide, and selenide has been drawn by considering all possible geometries by means of the semiempirical EH-MO method. In particular, the present results point to the following conclusions:

1. The most stable conformation is predicted to be a "butterfly" structure with twist angles of 52° for Ph_2O and of 38° both for Ph_2S and Ph_2Se.

2. The very small values calculated for the potential energy barriers allow for easy interconversion of the "enantiomers" and thus support the hypothesis of non-rigid structure for the molecules Ph_2X.

3. In Ph_2O the conversion of the preferred geometry into its enantiomer is most easily accomplished through a transition state of type B. In Ph_2S and Ph_2Se the corresponding transformation is estimated to proceed *via* a transition state of type C.

4. The contribution of 3d sulphur orbitals turns out to be ineffective in determining the ground-state conformation of diphenyl sulphide.

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