

## A CNDO/2 Study of the Mechanism of Isomerization and Conformation of Azobenzene

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A comparative study of the isomerization barrier between *cis*- and *trans*-azobenzene by two different mechanisms has been undertaken using the CNDO/2 method. One mechanism is a rotation around the N–N double bond and has an activation energy of 70.0 kcal/mol, whereas the other mechanism, *i.e.*, by inversion in the plane of the molecule, gave a considerably lower activation energy, 32.7 kcal/mol. This suggests that inversion should be the preferred mechanism of isomerization, in agreement with what is believed to be the case for the corresponding azomethine compounds.<sup>1-3</sup>

A calculation of the equilibrium conformations of *cis*- and *trans*-azobenzene was performed simultaneously and yielded the interesting result that the lowest energy of *trans*-azobenzene is that of the conformation, in which both phenyl rings are at right angles to the plane of the central double bond. The result is discussed in relation to available experimental evidence.

The question of the mechanism of isomerization about azo bonds has attracted considerable attention owing to its great photochemical and general interest. In particular, the question whether the isomerization proceeds *via* a rotation about the N–N double bond or by inversion in the plane of the double bond has been the subject of many discussions.

It was inferred that the lately developed CNDO method<sup>4-8</sup> would form a suitable basis for a further study of this question owing to its innate capability of handling nonplanar conformations and fairly large molecules.

From a more general point of view, the CNDO method shows promise of becoming a very valuable tool in the hands of the organic chemist. The validity of its approach to different types of problems therefore deserves careful study.

The CNDO/2 method was applied in the version described by Santry.<sup>8</sup> The phenyl rings of azobenzene were assumed to be regular hexagons with C–C distances equal to 1.39 Å, and C–H distances equal to 1.084 Å. The length of the central N–N double bond was assumed to be 1.230 Å in agreement with X-ray diffraction data,<sup>9</sup> and the N–C distance was set equal to 1.410 Å, unless otherwise stated. The designation of the atoms and angles of the molecule is shown in Fig. 1.

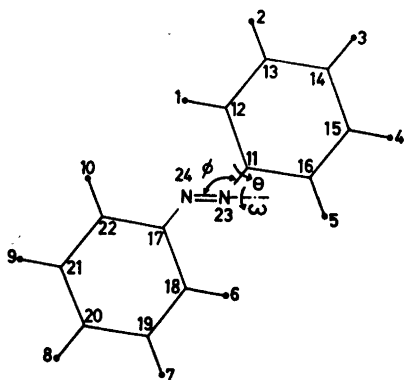


Fig. 1. Designation of angles and atoms in the azobenzene molecule.

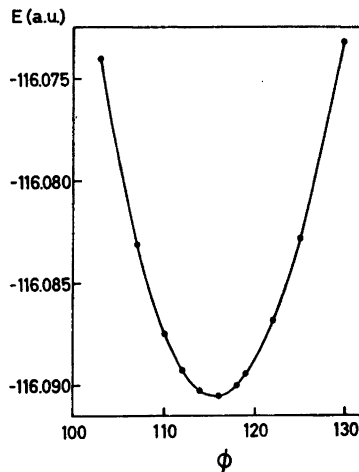


Fig. 2. Energy of planar *trans*-azobenzene when the angles denoted by  $\phi$  are varied symmetrically.

## RESULTS

*Ground state conformations.* In Fig. 2, the energy of *trans*-azobenzene is plotted as a function of the angle  $\phi$ , assuming a planar symmetrical conformation. The value obtained for the equilibrium angle is close to  $116^\circ$ , which is somewhat less than the value ( $121^\circ$ ) obtained for *trans*-azobenzene in the solid state, using X-ray diffraction techniques.<sup>9</sup> The deviation could be due to intermolecular interactions in the solid state; however, experimental evidence available at present does not allow a decision to be reached as to whether this represents a real difference or merely is the result of shortcomings of the CNDO-calculations.

Keeping  $\phi$  fixed at  $116^\circ$ , the two phenyl rings were then simultaneously rotated in a propeller-like fashion, until, in the end position, they were perpendicular ( $\theta = 90^\circ$ ) to their original direction (Fig. 3). Surprisingly, the CNDO calculation predicts the energy to be lower in the perpendicular conformation by approx. 5.5 kcal/mol. However, since the energy minimum at  $\theta = 90^\circ$  is extremely shallow, appreciable thermal oscillations would be expected to take place around such an equilibrium configuration. The calculations illustrated in Fig. 4 were undertaken in order to find out whether the equilibrium angle  $\phi$  would have the same value for the perpendicular conformation as for the planar one. In this case (for  $\theta = 90^\circ$ ), an energy minimum is obtained at  $\phi = 114.4^\circ$ . Thus, according to these calculations, the stable conformation of the molecule would be one in which the two phenyl rings are perpendicular to the plane of the N-N double bond and with the angle  $\phi = 114.4^\circ$ . The energy of this conformation is  $-116.09950$  a.u. The validity of this result will be discussed in the final section of this paper.

Fig. 5 shows the energy of *cis*-azobenzene as a function of the angle  $\theta$  when both phenyl rings were rotated by the same angle in a propeller-like fashion.

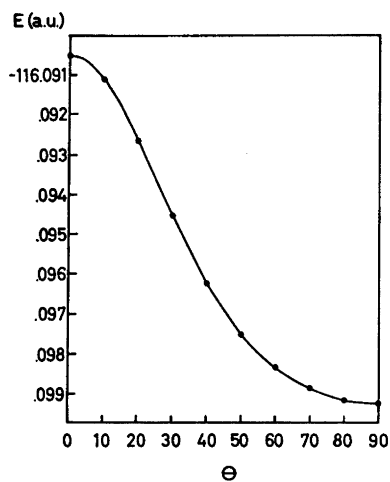


Fig. 3. Energy of *trans*-azobenzene when the phenyl rings are rotated by an angle  $\theta$  in a propeller-like fashion. The angles  $\phi$  of both halves of the molecule were  $116.0^\circ$ .

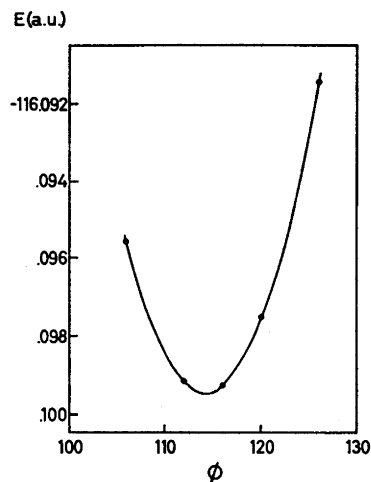


Fig. 4. Energy of perpendicular *trans*-azobenzene when the angles  $\phi$  are varied symmetrically.

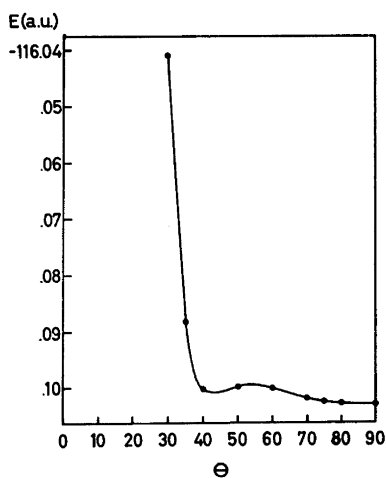


Fig. 5. Energy of *cis*-azobenzene when both phenyl rings are rotated by an angle  $\theta$  in a propeller-like fashion.  $\phi$  was set equal to  $116.0^\circ$  for both halves of the molecule.

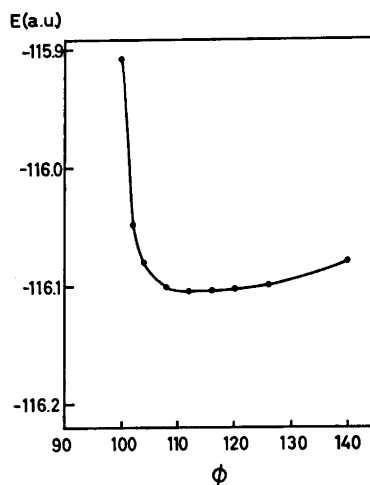


Fig. 6. Energy of perpendicular ( $\theta = 90.90$ ) *cis*-azobenzene when both angles  $\phi$  were varied in a symmetrical manner.

The angle  $\phi$  was set equal to  $116.0^\circ$ . The diagram shows the existence of two shallow energy minima, one at  $\theta = 44^\circ$ , and one at  $\theta = 90^\circ$ , separated by an energy barrier of approx. 1 kcal/mol. The minimum at  $\theta = 90^\circ$  is about 1 kcal/mol lower than that at  $\theta = 44^\circ$ . Keeping  $\theta$  fixed at  $90^\circ$ , the angles  $\phi$  of both halves of the molecule were then varied. (Fig. 6). The curve shows a fairly shallow energy minimum at  $\phi = 112^\circ$  with  $E = -116.103585$  a.u. Thus, the energy of the *cis* conformation is 0.00409 a.u. or 2.6 kcal/mol lower than that of the *trans*-conformation. Continued decrease in  $\phi$  leads to a decrease in energy, implying bonding between the two phenyl rings. This bonding is obviously fortuitous in that it only reflects the lack of differential overlap in the CNDO-method.

*Isomerization barrier.* One of the main purposes of this work was to establish the most probable mechanism for the isomerization of azobenzene. Previous investigations have pointed out the theoretical possibility of two different mechanisms of isomerization. One is a rotation about the N–N double bond, and the other can be described as an inversion at one of the nitrogen atoms taking place in the plane of the molecule.

Fig. 7 shows the variation of energy when the molecule is rotated about the N–N double bond with the angles  $\phi$  and  $\theta$  being held constant at  $116^\circ$  and  $90^\circ$  degrees, respectively, for both halves of the molecule. The top of the barrier corresponds to  $E = -115.992101$  a.u. Fig. 8 shows the corresponding

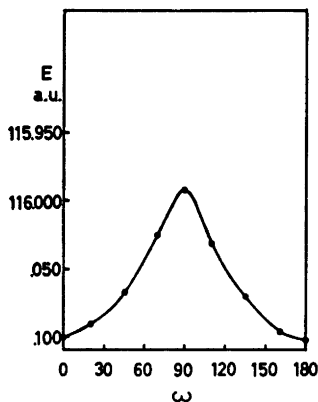


Fig. 7. Rotational isomerization of azobenzene;  $\omega$  denotes the angle of rotation. The angle  $\phi$  was equal to  $116.0^\circ$  for both halves of the molecule.

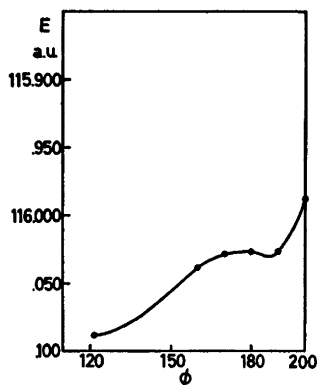


Fig. 8. Incomplete isomerization by inversion of planar azobenzene. The *cis* equilibrium conformation is never reached owing to steric hindrance, which causes the energy to rise for  $\phi > 185^\circ$ . The angle  $\phi$  was equal to  $121.5^\circ$  for the left half of the molecule.

curve when the inversion mechanism is active. In this case, the left half of the molecule was held fixed at  $\phi = 121.5^\circ$ , while  $\phi$  for the right half was being varied. The curve shows a sharp rise almost immediately to the right of the top of the barrier, owing to sterical contact between hydrogen atoms. In order to avoid this, the corresponding curve was also calculated for the case where both

phenyl rings are perpendicular to the plane of the central double bond (Fig. 9). As before, the angle  $\phi$  for the left half of the molecule was  $116^\circ$ . In addition to avoiding the complication of sterical interaction, this conformation also gives a somewhat lower inversion barrier.

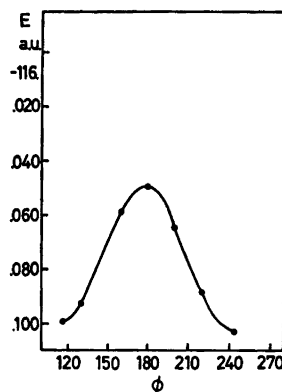


Fig. 9. Isomerization of perpendicular azobenzene by inversion. The angle  $\phi$  was equal to  $116.0^\circ$  for the left half of the molecule, while  $\phi$  for the right half of the molecule was being varied as shown.

To avoid excessive calculation, the energy of the *cis* and *trans* equilibrium conformations were not minimized with respect to variations of the N–N and N–C bond distances. However, such a variation was performed at the top of the inversion barrier, partly because it was suspected that the energy of this conformation might be more sensitive to such a variation, and partly because it was anticipated that the lengths of the bonds in the transition state would be different from those of the equilibrium conformations. Table 1 shows the results of these calculations. The lowest energy for the top of the barrier was obtained for  $\theta = 90^\circ$ ;  $\phi$  for the left half of the molecule =  $116.0^\circ$ , N–N distance =  $1.230 \text{ \AA}$ , and N–C distance =  $1.390 \text{ \AA}$ , and it amounted to  $-116.051461 \text{ a.u.}$

Table 1. Energy (in a.u.) at the top of the inversion barrier for different values of the N–N and N–C distances. For the left half of the molecule,  $\phi$  is equal to  $111.0^\circ$  (upper line),  $114.4^\circ$  (middle line), and  $116.0^\circ$  (lower line).

		N–N distance		
		1.230	1.260	1.300
N–C distance	1.410	– 116.048311	– 116.045259	– 116.031426
		– 116.049023	– 116.045709	–
		– 116.049125	– 116.045709	–
	1.390	– 116.050450	– 116.047728	– 116.034292
		– 116.051291	– 116.048306	– 116.034543
		– 116.051461	–	–
	1.370	– 116.049185	– 116.046808	– 116.033788
		– 116.050167	– 116.047524	– 116.034176
		–	–	–

The activation energies were calculated to be 70.0 kcal/mol and 32.7 kcal/mol for rotation and inversion, respectively, using the energy of the minimum energy, *cis* equilibrium conformation as a reference and neglecting the small zero point energy of vibration. The experimental value is 23 kcal/mol.<sup>10</sup>

#### DISCUSSION

According to the calculations reported, inversion would be the most probable mechanism of isomerization since it involves the lowest activation energy. The validity of this result is, however, difficult to assess. The value obtained for the inversion barrier in *N*-benzylideneaniline appears to be in reasonable agreement with experimental results.<sup>2</sup> It is also of interest to note that in the case of *N*-benzylideneaniline, CNDO predicts a lower barrier for inversion than for rotation about the central C–N double bond. Similar results were obtained by Lehn and Munsch in their *ab initio* SCF-LCAO-MO study of the isomerization barrier of methylenimine.<sup>3</sup>

According to the CNDO calculations, *trans*-azobenzene would have its lowest energy in the conformation where both phenyl rings are perpendicular to the plane of the central N–N double bond. As was already pointed out above, the calculations yield a lower energy for this conformation (by 5.5 kcal/mol) than for the planar molecule.

This result is in direct opposition to the current view that the *trans*-azobenzene molecule is planar. This view seems to be based mainly on X-ray crystallographic investigations of solid *trans*-azobenzene<sup>9</sup> and on the conspicuous similarity between the UV-visible spectra of *trans*-azobenzene and *trans*-stilbene.<sup>11</sup> The fact that the energy of crystalline *trans*-azobenzene is from 9 to 12 kcal/mol lower than that of crystalline *cis*-azobenzene<sup>12,13</sup> also seemed to corroborate this opinion. The lower energy of the *trans* form is consistent with the assumption of a strong stabilization of the planar form owing to resonance interaction ( $\pi$ – $\pi$  conjugation). This assumption of a delocalization energy of a sufficient magnitude is well in line with the results of earlier quantum chemical calculations. Thus, the Hückel MO method gives a resonance energy of 15.5 kcal/mol for planar *trans*-azobenzene.<sup>14</sup>

Quite irrespective of the question of the validity of the present CNDO calculations it is obvious that the available experimental data about azobenzene are rather incomplete. In particular it should be stressed that the quantum chemical calculations refer to free molecules, which makes a comparison with gas phase data most natural. Unfortunately, to the authors' knowledge, no direct conformational studies of azobenzene in the gas phase have so far been performed. The more indirect data which are available, *e.g.* UV-visible spectra in the gas phase, are rather incomplete and of poor quality.<sup>15</sup>

The well-known case of biphenyl offers a good illustration of the necessity for exercising a good deal of discretion when one attempts to draw conclusions about the behaviour of free molecules from data obtained in experimental studies on the liquid or solid state. According to the X-ray crystallographic studies, biphenyl has a planar conformation in the solid state,<sup>16,17</sup> whereas, according to electron diffraction studies, in the gas phase the free molecule has an angle of approx. 45° between the two phenyl rings.<sup>18–20</sup> In addition to

this, biphenyl in heptane solution is estimated to have an angle of approx.  $20^\circ$  between the phenyl rings according to spectrophotometric evidence.<sup>11</sup> This possibly indicates a strong solvent effect on the conformation. Similar effects could not *a priori* be excluded for other substances either.

As is well known, the CNDO method is based upon a number of approximations and it is also rather sensitive to the choice of parametrization. This necessitates a certain amount of discretion in interpreting the results of such calculations. On the other hand, this method has an innate capacity for handling cases of non-planar molecules and non-bonded interactions which were not directly attainable by earlier methods. A final decision as to the validity of the results of the calculations will, of course, have to be based on direct experimental observations or on more profound theoretical considerations.

The results of earlier CNDO calculations on *N*-benzylideneaniline<sup>2</sup> and stilbene<sup>21</sup> are, in general, consistent with the results reported here. With the same parametrization applied in all three cases, the CNDO method predicts that, apart from possible steric hindrance, a phenyl ring attached to a carbon atom should be almost free to rotate, whereas a phenyl ring attached to a nitrogen atom is non-planar with respect to the rest of the molecule owing to an additional barrier to rotation. The difference in behaviour in the latter case may be due to the possibility of the free electron pair of the nitrogen atom conjugating with the  $\pi$ -electrons of the phenyl ring ( $n-\pi$  conjugation). Of course, the predicted absence of a rotational barrier in the former case also remains to be explained.

It is difficult to decide whether the CNDO method overestimates the extent of  $n-\pi$  conjugation compared with the extent of  $\pi-\pi$  conjugation. However, the fact that *N*-benzylideneaniline is generally considered to be nonplanar seems to indicate that the effects of the two types of conjugation could be comparable in magnitude. Bürgi and Dunitz<sup>22</sup> ascribe the non-planar conformation of *N*-benzylideneaniline to steric hindrance due to contact interaction between hydrogen atoms, but their conclusion is based on calculations using the simple HMO-method, according to which the  $\pi$ -electron energy of the planar conformation would be 6 kcal/mol lower than for the perpendicular one. Since the true delocalization energies for the two types of conjugation are not known, the possibility of a certain degree of twisting of the phenyl rings of the free *trans*-azobenzene molecule cannot *a priori* be excluded. The large energy difference, mentioned above, between *cis*- and *trans*-azobenzene in the solid state does not necessarily contradict the possible non-planarity of the *trans*-isomer, since it could very well be due to intermolecular interactions, specific for the solid state.

When interpreting the results of the CNDO calculations, one should also keep in mind that the calculations predict the *cis*-isomer to be more stable than the *trans*-isomer by 2.6 kcal/mol. This is contrary to all experimental evidence.

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