

A GAS ELECTRON DIFFRACTION STUDY OF THE MOLECULAR STRUCTURE OF *TRANS*-AZOBENZENE

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(Received 20 December 1976)

ABSTRACT

The molecular structure of *trans*-azobenzene has been studied by the gas electron diffraction method. The molecule was found to have a non-planar conformation with the phenyl groups twisted approximately 30° around the N— Φ bonds. It was, however, not possible to decide whether the phenyl groups were rotated to the same or to the opposite side of the planar ethylene group.

INTRODUCTION

The present study is part of our endeavour to clarify the molecular properties of conjugated molecules with aromatic rings as part of the conjugated system. These studies so far include investigations of *cis*-stilbene [1], *trans*-stilbene [2], *N*-benzylideneaniline [3] and styrene [4]. Efforts were also made to study the molecular structure of *cis*-azobenzene, but the compound isomerized too quickly to the *trans* isomer for an investigation to be undertaken at the temperature necessary for sufficient vaporization. The molecular structure of *trans*-azobenzene was first studied by Robertson [5] in 1939 by X-ray crystallography. He found the molecule to be essentially planar and his results were confirmed by Brown [6] in a similar study nearly 30 years later.

Ortho-substituted azobenzenes have been studied in the liquid phase by Gore and Wheeler [7] and by Yamamoto et al. [8], using UV-spectroscopy. They found the molecules to deviate somewhat from planarity. The N—C dihedral angles were found to be in the region 20 – 40° . These observed distortions from planarity may however be due to interferences between the *ortho* substituent and the rest of the molecule.

The molecular structure of *trans*-azobenzene has also been studied by CNDO/2 calculations by Ljunggren and Wettermark [9]. Their calculations gave C—N dihedral angles of 90° , corresponding to a structure where the phenyl ring is perpendicular to the C—N=N—C plane.

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EXPERIMENTAL

A commercial sample of *trans*-azobenzene from Aldrich Chem. Co. was used in the present study. The sample was claimed to have a purity of 99.9% or better, and was used without further purification. The electron diffraction pattern from the gas was recorded on the electron diffraction unit at Oregon State University. The nozzle tip temperature varied between 162 and 199°C during the exposures. The electron wavelength was 0.05749 Å, corresponding to an accelerating potential of about 43.6 kV. Exposures were made at nozzle to photographic plate distances of 120.808, 299.808 and 749.714 mm. The number of plates from each of these distances was 4, 3 and 3, respectively. The experimental data were processed in the usual way [10], and the resulting molecular intensity function extended from $s = 1.00 \text{ Å}^{-1}$ to $s = 46.25 \text{ Å}^{-1}$, with $\Delta s = 0.25 \text{ Å}^{-1}$.

The final experimental molecular intensity function is shown in Fig. 2. The intensities were modified by $s|f'_C|^{-2}$. The scattering amplitudes (f') were calculated by the partial-wave method [11], using Hartree—Fock atomic potentials [12].

The radial distribution RD curve obtained by Fourier transformation [10] of the final experimental intensity curve is shown in Fig. 3.

STRUCTURE ANALYSIS

A molecular model of *trans*-azobenzene which gives the numbering of the atoms is shown in Fig. 1.

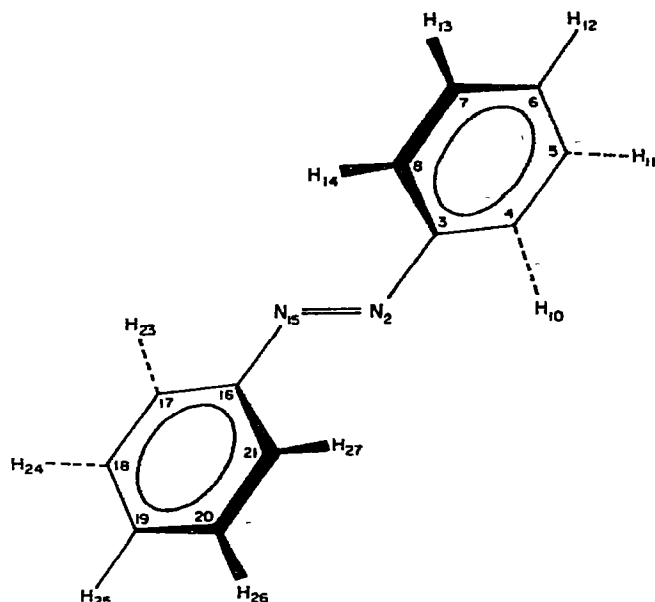


Fig. 1. Molecular model of *trans*-azobenzene which shows the numbering of the atoms.

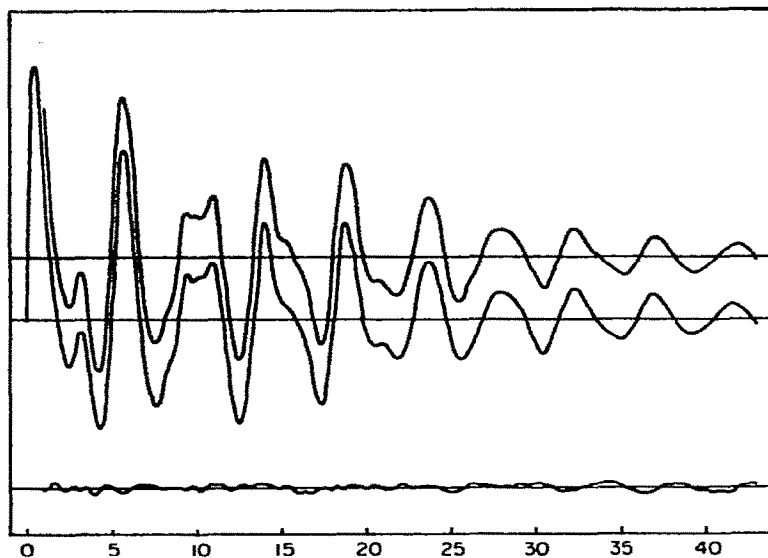


Fig. 2. Experimental and theoretical molecular intensity functions of *trans*-azobenzene (model C_2) and the differences between the two.

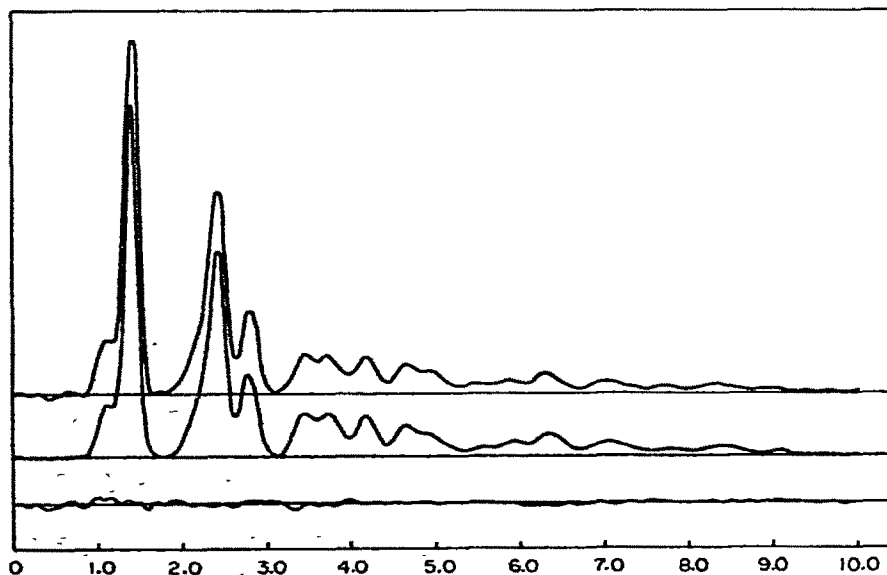


Fig. 3. Experimental and theoretical radial distribution function of *trans*-azobenzene (model C_2) and the differences between the two.

The molecular structure of *trans*-azobenzene was studied by least squares analyses of the molecular intensity function. In order to calculate theoretical molecular intensity functions for use in the analyses, it is necessary to know the vibrational amplitudes for all interatomic distances. In principle these

quantities are accessible from an electron diffraction experiment. In a large molecule like *trans*-azobenzene, which has a multitude of overlapping peaks in the RD function, it is, however, difficult to obtain reliable experimental values for many of the vibrational amplitudes. These quantities were therefore calculated from an assumed force field [13–15], using Gwinn's method [16, 17]. These calculations also give the correction coefficients necessary for determining an R_α structure. R_α is defined as the distances between average positions of the atoms, and an R_α structure is therefore geometrically consistent. It is especially advantageous to determine an R_α structure in the present case where fairly large shrinkage effects might otherwise be expected.

Trans-azobenzene is a large molecule to be studied by gas electron diffraction and in the refinements it was necessary to make certain assumptions about the structure. The phenyl rings were assumed to have a planar hexagonal structure which were rotated to the same degree about the C–N bonds. Coplanarity of the C–N=N–C group was further assumed.

Two different models of *trans*-azobenzene were studied. In model I the phenyl groups were rotated in opposite directions, corresponding to C_1 symmetry, while in model II the phenyl groups were rotated in the same direction, corresponding to C_2 symmetry.

When the assumptions given above were applied, the geometry of each of the two models was determined by seven parameters. These include four bond lengths (N=N, N–C, C–C and C–H), two valence angles (\angle N=N–C and \angle N₂–C₃–C₈) and the N=N–C₃–C₈ dihedral angle ($\angle\Phi$). All the geometrical parameters could be refined simultaneously in the least squares analyses for both models. The results of the least squares analyses based on R_α structures are presented in Table 1 for both models. The RD curves for both models are shown in Figs. 3 and 4 together with the experimental RD curve.

Table 2 gives the nonbonded carbon–carbon and carbon–nitrogen distances for model 1. The calculated vibrational amplitudes $u^{\text{calc.}}$ are also given, together with amplitudes determined from the electron diffraction data u^{ED} . Where no value is given in the u^{ED} column the calculated u -value has been applied. The corresponding data for model 2 are not presented here, but they are available upon request from the authors.

It was not possible to refine the vibrational amplitudes of all bond distances simultaneously in the least squares analyses. $u(\text{N–C})$ and $u(\text{C–H})$ were varied together with the geometrical parameters, while $u(\text{C–C})$ in the phenyl rings were kept at the calculated value (0.0463 Å). $u(\text{N=N})$ was determined by varying this parameter continuously over the expected range while the geometrical parameters were refined in the least squares analyses.

Some of the vibrational amplitudes of nonbonded distances were also determined in the least squares analyses. They were refined individually together with the geometrical parameters and the results are given in Table 2.

TABLE 1

Geometrical parameters and vibrational amplitudes for *trans*-azobenzene as resulting from least squares refinements

(The numbers in parentheses are assumed values or standard deviation values from the least squares analyses. The bond distances are given as R_a values.)

	I ^a	II ^b
N=N (Å)	1.259 (4)	1.268 (4)
N—C (Å)	1.420 (4)	1.427 (4)
C—C (Å)	1.396 (1)	1.396 (1)
C—H (Å)	1.082 (3)	1.088 (3)
∠N=N—C (°)	116.0 (.4)	114.5 (.4)
∠N ₁ —C ₁ —C ₂ (°)	121.2 (.5)	123.0 (.5)
∠Φ (°)	30.1 (1.6)	27.9 (2.9)
$u(\text{N}=\text{N})$ (Å)	(0.0460)	(0.0460)
$u(\text{N}-\text{C})$ (Å)	0.0655 (40)	0.0613 (43)
$u(\text{C}-\text{C})$ (Å)	(0.0463)	(0.0463)
$u(\text{C}-\text{H})$ (Å)	0.0739 (28)	0.0752 (27)
$\sum w_i \Delta_i^2$	$0.124 \cdot 10^3$	$0.123 \cdot 10^3$
i		

^aI Model with C_2 symmetry.

^bII Model with C_i -symmetry.

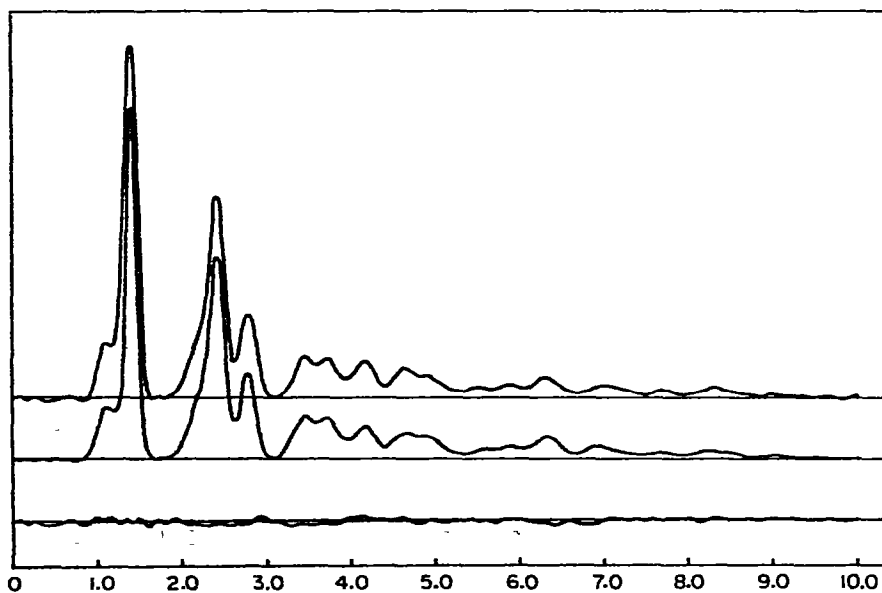


Fig. 4. Experimental and theoretical radial distribution function of *trans*-azobenzene (model C_1) and the differences between the two.

TABLE 2

Nonbonded CN and CC distances for model I of *trans*-azobenzene (C_2 -symmetry)
(The vibrational amplitudes u^{calc} are those calculated from an assumed force field, while u^{ED} are those obtained in the electron diffraction study.)

	r	u^{ED}	$u^{\text{calc.}}$		r	u^{ED}	$u^{\text{calc.}}$
N_2C_{16}	2.266		0.0760	C_3C_{20}	5.514	0.125	0.1343
C_3C_5	2.415	0.068	0.0587	C_4C_{17}	5.705	0.105	0.0945
N_2C_4	2.420		0.0685	C_3C_{18}	5.892		0.0953
N_2C_{21}	2.762		0.1292	C_7C_{21}	6.258		0.1289
C_3C_6	2.791	0.060	0.0652	C_3C_{19}	6.260	0.120	0.1659
N_2C_{17}	3.474	0.078	0.0825	C_4C_{20}	6.372		0.2166
C_3C_{16}	3.557	0.083	0.0773	C_6C_{21}	6.891		0.1521
N_2C_5	3.700		0.0691	C_4C_{18}	6.904		0.1361
N_2C_{20}	4.127		0.1301	C_4C_{19}	7.189		0.1649
C_3C_{21}	4.138	0.111	0.1342	C_7C_{20}	7.625		0.1259
N_2C_6	4.207	0.077	0.0710	C_5C_{20}	7.715		0.2078
C_3C_{17}	4.630	0.122	0.1014	C_2C_{18}	8.161		0.0999
N_2C_{18}	4.632	0.122	0.0935	C_6C_{20}	8.267		0.1501
N_2C_{19}	4.894	0.110	0.1135	C_5C_{19}	8.517		0.1451
C_6C_{21}	4.896		0.1276	C_6C_{19}	8.993		0.1146
C_4C_{21}	5.047	0.130	0.1014				

DISCUSSION

In Table 3 the geometrical parameters determined for *trans*-azobenzene are compared to results obtained for structurally related molecules. The N=N distance is found to be somewhat large compared to other distances of this kind, while the C—N distance is observed to be about the same as determined by X-ray crystallography [6]. The C—N distances cannot be compared to those of the aliphatic azo compounds, where these distances will naturally be larger because of the different state of hybridization of the carbon atoms.

The determined N=N—C valence angle is significantly smaller than 120° , which is the valence angle corresponding to sp^2 hybridization of the nitrogen orbitals. This is in agreement with what is observed for other azo compounds, as will be seen from Table 3. It may be expected to be energetically favourable with a larger percentage s character in the lone-pair orbital than in those participating in the σ -bonds. Such a hybridization situation will give valence angles smaller than 120° at the nitrogen atoms. If the N=N π -bond is a result of overlapping p -orbitals with no s character and the N orbitals participating in the σ -bonds are assumed to have identical hybridization states, a N=N—C angle of 114.5° corresponds to 29% s character in the bonding orbitals and 42% s character in the lone-pair orbital.

The present study shows that *trans*-azobenzene has a non-planar conformation in the gas phase, with phenyl groups twisted about 30° around

TABLE 3

Comparison of the structural parameters of *trans*-azobenzene with those of structurally related molecules

Molecule	Method	N=N (Å)	C-N (Å)	C-C (Å)	∠N=N-C	∠N-C-C	∠Φ	Ref.
<i>trans</i> -Azobenzene	ED	1.259	1.420	1.396	116.0°	121.2°	30.1°	Present study C ₂ -structure
<i>trans</i> -Azobenzene	ED	1.268	1.427	1.396	114.5°	123.0°	27.9°	Present study C ₁ -structure
<i>trans</i> -Azobenzene	X-ray	1.243	1.433	1.365-1.385	113.6°	124.1°	0°	6
<i>trans</i> -Azobenzene	CNDO/2				114.4°		90°	9
Azomethane	ED	1.247	1.482					19
Hexafluoroazomethane	ED	1.236	1.489		112.0° 126/110°			20
Methyl azotrifluoromethane	ED	1.253	1.474		112.0°			20
<i>trans</i> -Stilbene	ED			1.398			30°	2
2,2'-Disubstituted azobenzene	UV						18-35°	7
2,2'-Disubstituted azobenzene	UV						20-40°	8

the C—N bonds. It is, however, not possible to decide between models with C_i and C_2 symmetry, corresponding to phenyl rings rotated in the opposite or in the same direction. It is possible that both conformers are present in the gas phase.

There are not many experimental data available that might support the observed non-planarity of *trans*-azobenzene. Yamamoto et al. [8] have studied the electric dipole moments of several substituted *trans*-azobenzenes in solution. They find in all cases that the phenyl groups are twisted around the C—N bonds, but they were not able to decide whether the phenyl groups are twisted in the same or in the opposite direction. The same research group [18] has later determined the crystal and molecular structure of *trans*-2,2'-dichloroazobenzene where they determined the C—N dihedral angle to be 12.8° . As the molecule was found to have a centre of symmetry, the phenyl groups must be symmetrically twisted relative to the azo group. These results are however not directly comparable to those obtained in the present study, as the preferred conformation might be due to intermolecular forces present in the crystal state.

In *trans*-azobenzene there may be contribution to the π -electron energy by interaction of the nitrogen lone-pair electrons with the π -electrons of the phenyl rings. A twist around the C—N bonds is expected to reduce the π — π interaction and increase the n — π interaction. The magnitude of the n — π interaction energy is to a large degree dependent on the location of the nitrogen lone-pair orbital. If the nitrogen orbital participating in the N=N π bond has a small percentage s character, the lone-pair orbital may be bent away from the C—N=N—C plane thereby increasing the n — π interaction energy.

The *trans*-stilbene molecule [2] was also found to have a non-planar conformation in the gas phase with the phenyl groups twisted about 30° out of the plane of the central ethylene group. In *trans*-stilbene the deviation from planarity might be ascribed to nonbonded interaction. In *trans*-azobenzene the nonbonded interaction is however considerably smaller than in *trans*-stilbene. The preferred conformation of *trans*-azobenzene might therefore possibly be mainly due to interactions between the lone-pair electrons and π electrons in the phenyl rings.

ACKNOWLEDGEMENTS

The authors wish to thank Dr. Kenneth Hedberg, Oregon State University, for placing his electron diffraction laboratory at their disposal. Financial support from Norges almenvitenskapelige forskningsråd is gratefully acknowledged.

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