

Article

# Comprehensive Study of Equilibrium Structure of Trans-Azobenzene: Gas Electron Diffraction and Quantum Chemical Calculations

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**Abstract:** The geometrical  $r_e$  parameters of trans-azobenzene (E-AB) free molecule were refined by gas electron diffraction (GED) method using available experimental data obtained previously by S. Konaka and coworkers. Structural analysis was carried out by various techniques. First of all, these included the widely used molecular orbital constrained gas electron diffraction method and regularization method. The results of the refinements using different models were also compared—a semirigid model, three variants of one-dimensional dynamic models, and a two-dimensional pseudoconformer model. Several descriptions have been used due to the fact that E-AB has a shallow potential energy surface along the rotation coordinates of phenyl groups. Despite this, it turned out that the semirigid model is suitable for use for E-AB and allows good agreement with experimental data to be achieved. According to the results of GED structural analysis, coupled with the results of DLPNO-CCSD(T0) calculations, E-AB has a planar structure. Based only on GED data, it is impossible to unambiguously determine the rotational angle of the phenyl group due to the facts that (i) with rotation over a wide range of angles, the bonded distances in the molecule change insignificantly and (ii) potential function in a structural analysis within a dynamic model is not determined with the necessary accuracy. This work also examines the sensitivity of the GED method to structural changes caused by trans-cis isomerization. The paper also analyzes the applicability of different variants of density functional theory (DFT) calculations in GED structural analysis using E-AB as an example. There are not enough similar methodological works in the literature. This experimental and methodological information is especially important and relevant for planning and implementing GED experiments and corresponding processing of the results for azobenzene derivatives, in which the conformer and isomeric diversity are even more complicated due to the presence of different substituents.

**Keywords:** gas-phase electron diffraction; molecular structure; quantum chemistry; azobenzene; pseudoconformer



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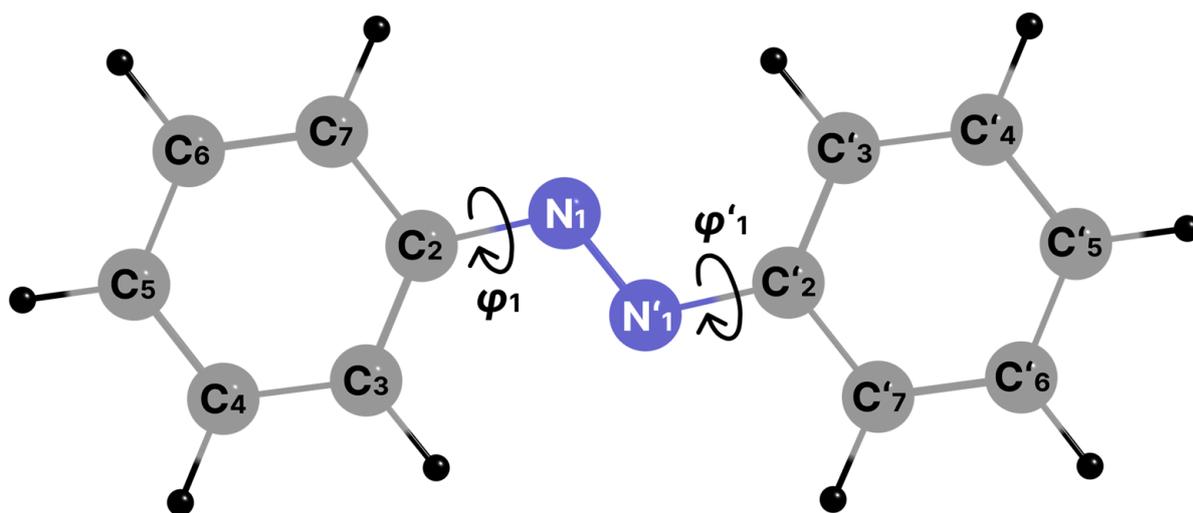
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## 1. Introduction

Azo compounds  $R_1-N=N-R_2$ , and especially azobenzenes, receive much attention as promising compounds for creating functional and “smart” materials [1,2]. Perhaps the main object of research in this area is photoisomerization ( $\text{trans} \rightleftharpoons \text{cis}$  or  $E \rightleftharpoons Z$ ), which makes azo compounds suitable for use in a different range of applications, such as the

development of various sensors, molecular switches, optical data storage, nonlinear optics, color-changing materials [3–8], etc. Of course, much attention is paid to modifying these compounds by adding special functional groups [9–13]. In this regard, structural studies play a huge role in describing and predicting physicochemical properties. It is logical and self-explanatory that the “parent” azobenzene (AB) has been the subject of plenty of structural and spectral studies.

The current consensus is that E-AB (Figure 1) is characterized by a flat structure. However, the planarity of the E-AB structure has been the subject of controversial studies. There were several articles [14,15] describing azobenzene as a distorted molecule and many more modern works [16–22] proving the planar structure of the E-AB molecule. At the same time, in the crystalline state and in solutions, these molecules can undergo significant distortions [23–27]. It should be noted that structures in the solid and liquid phases are usually distorted due to intermolecular interactions. Structures determined by the gas electron diffraction (GED) method do not suffer from these interactions and reflect the properties of a free molecule. The first interpretation of the results of the GED experiment for AB was carried out in 1977 by Traetteberg and coworkers [28]. According to their interpretation, the molecule E-AB in the gas phase is nonplanar and phenyl groups twisted about  $\varphi \approx 30^\circ$ . Also, the authors of ref. [28] suggested that there are two conformers of  $C_i$  and  $C_2$  symmetries corresponding to phenyl rings rotated in the opposite and in the same direction, respectively. Vibrations corresponding to rotations of phenyl rings ( $A_u$  and  $B_g$  irreducible representations under  $C_{2h}$  point group) have frequencies of 15–21 and 95–111  $\text{cm}^{-1}$  [19,20]. Potential energy surface (PES) of E-AB is shallow along the N=N-C-C torsional coordinates [19]. Studying the consequences of conformations in diffraction, the authors of ref. [29] came to the conclusion that for trans-stilbene (an E-AB-like molecule) and other molecules with flat PES, the pseudoconformer approach must be used to properly describe the diffraction pattern. In 2001, Konaka and coworkers [30] repeated the GED experiment for E-AB and interpreted their results within the framework of a dynamic model constructed using pseudoconformers: the stable form of E-AB was found to be planar. In that structural analysis, data from MP2/6-31+G\* calculations were used, according to which the minimum on the PES corresponds to a distorted structure. Apparently, it is an artifact resulting from the use of a deficient ab initio approach [19,29].



**Figure 1.** Structure and atom labels of E-AB.  $\varphi_1$  and  $\varphi'_1$  are torsion angles  $N'_1-N_1-C_2-C_3$  and  $N_1-N'_1-C'_2-C'_3$ .

Quantum chemical (QC) calculations are powerful tools for the determination of molecular structure and specificity of intramolecular dynamics. Nowadays, a lot of variants of approaches to the solution of such problems based on both ab initio and density functional theory (DFT) methods have been created. The method of coupled clusters can

be called the most preferable at the moment. However, such calculations are very computationally expensive and realistically applicable only for molecules with a small number of atoms. Far less computationally expensive DFT methods can serve as an alternative but choosing the optimal functional/basis set combination from the many existing variants is a challenging task.

The structure determined experimentally by GED is of indisputable value. The experimental data available in the literature [30] operate with thermal averaged distances  $r_g$ , but these parameters are trigonometrically inconsistent and cannot be directly compared with parameters determined by QC calculations [31]. The transition from the experimentally observed thermally average structure to the equilibrium structure requires solving the problem of accounting for the specificity of intramolecular dynamics. This work considers the issue of the applicability of QC data obtained by various DFT functionals in structure refinement using GED data. In general, the choice of one or another DFT functional should not affect the structural analysis. However, under GED structural refinement for large molecules, nonvariable vibrational corrections  $r_e - r_a$  (or  $r_{h1} - r_a$ ) and nonvariable differences between the nonequivalent structural parameters in case of the MOCED (molecular orbital constrained gas electron diffraction) method [32] may influence the final results. The purpose of this work is to determine the equilibrium structure of the E-AB in terms of  $r_e$  parameters. Experimental data (molecular scattering intensities and background function) for the corresponding analysis were taken from [30]. It should be noted that in the works carried out twenty years ago and earlier (including ref. [28,30]), the  $r_e$  structures for medium-sized molecules were rarely determined due to the lack of the necessary computer power that is currently available. This information about  $r_e$  structural parameters of the “parent” molecule will be relevant for the subsequent comparison of experimentally and theoretically obtained structural parameters for substituted azobenzenes. A careful structural analysis of the parent AB is the first step toward planned studies of the gas phase molecular structure of phthalonitrile-based azodyes (e.g., [20]), in which the GED analysis will be further complicated by the need to consider tautomerism and a larger number of internal rotations. The present work also continues the studies [33–36] devoted to determining the sensitivity of the GED method to different kinds of conformational transitions caused by the rotation of various groups.

## 2. Methods

### 2.1. Computational Details

DFT calculations of the molecular geometries and Hessian of AB were performed using the Gaussian 09 program package [37]. To assess the applicability of the calculation results in the GED structural analysis, a large number of calculations were carried out using various DFT functionals—B3LYP [38,39], B97D [40], B98 [41], BMK [42], BP86 [43,44], CAM-B3LYP [45], LC- $\omega$ PBE [46–48], M05 [49], M06 [50], M06HF [51,52], mPW1PW91 [53], PBE0 [54], PBE [55], TPSSH [56,57], VSXC [58], and X3LYP [59]. The basis set pcseg-2 [60] from the Basis Set Exchange software [61] was used in all DFT calculations. These basis sets were optimized for use in the DFT theory and were recommended for using in geometry optimizations and calculations of energies, vibrational frequencies, etc. [62]. “Tight” optimization convergence criterion and an “ultrafine” grid (pruned, 99 radial shells and 590 angular points per shell) were used. In a recent paper [63], it was declared that empirical dispersion corrections are not beneficial for medium-sized carbene systems. This is also true for planar E-AB. For an adequate comparison of DFT functionals, it was decided not to use empirical dispersion corrections. Nevertheless, cubic force fields from B3LYP calculations with Grimme’s dispersion corrections D3 [64] were used to generate the starting internuclear distances, vibration amplitudes, and corrections ( $r_e - r_a$ ), which were utilized in the final GED structural analysis.

The domain-based local pair natural orbital coupled cluster method with single, double, and semicanonical perturbative triples corrections DLPNO-CCSD(T0) [65–68] with TightPNO thresholds was used for single-point (SP) energy calculations in the ORCA pro-

gram [69]. DLPNO-CCSD(T0) calculations were performed using corresponding optimized geometries from DFT/pcseg-2 calculations. SCF convergence was set to “VeryTight”. The calculations utilize correlation consistent basis sets cc-pVTZ [70] and cc-pVQZ [70]. The computational effort was reduced by making use of the resolution of the identity with the auxiliary basis sets cc-pVnZ/C ( $n = T, Q$ ) [71]. Equation (1) [72] was used for two-point complete basis set (CBS) extrapolations with cc-pVnZ ( $n = T, Q$ ) basis sets.

$$E_{DLPNO-CCSD(T0)}^n = E_{DLPNO-CCSD(T0)}^\infty + \frac{A}{(n + 1/2)^4} \quad (1)$$

where  $n = 3$  for cc-pVTZ and  $n = 4$  for cc-pVQZ,  $A$ —constant, determined by solving a system of two equations.

Fractional occupation number weighted density (FOD) calculations were also carried out using ORCA [69]. The FOD was conducted by finite-temperature DFT calculations with a smearing temperature of 5000K using a TPSS [56] functional and def2-TZVP [73] basis set, as recommended by the authors of ref. [74].

## 2.2. Structural Analysis

### 2.2.1. Approaches

The experimental data (molecular scattering intensities and background function) obtained by the authors of ref. [30] were used to carry out the structural analysis. The procedure of the GED data refinement was performed using the UNEX program [75]. The Z-matrix was constructed according to the  $C_{2h}$ -symmetry group (Table S1). Harmonic and cubic force fields were used for the generation of vibrational amplitudes and corrections ( $r_{h1} - r_a$  and  $r_e - r_a$ ) by the VibModule program [76]. We will call the obtained structural parameters semiexperimental, since the vibrational corrections to the equilibrium geometry have an exclusively theoretical nature. Two approaches of structure refinement were applied to refine the structural parameters: molecular orbital constrained gas electron diffraction (MOCED) [32] using Equation (2) and the regularization method (RM) [77–79] using Equation (3).

$$\Phi_{GED} = \sum_i \left( s_i M(s_i)^{exp} - s_i M(s_i)^{theor} \right)^2 \quad (2)$$

$$\Phi_{reg} = \Phi_{GED} + \alpha_{reg} \cdot \sum_k w_k \left( p_k^0 - p_k \right)^2 \rightarrow \min \quad (3)$$

where  $s_i M(s_i)^{exp}$ —experimental molecular scattering intensities from [30];  $s_i M(s_i)^{theor}$ —theoretical molecular scattering intensities;  $\alpha_{reg}$ —regularization constant;  $w_k$ —individual weight;  $p_k^0$ —reference (restraining) value; and  $p_k$ —the model (refining) value of the  $k$ -th structural parameter of the molecule.

For the MOCED variant, refinements were carried out in a way that parameter differences were constrained within sorted groups. Under the current study, four types of internuclear distances ( $N_1=N'_1$ ,  $N_1-C_2$ ,  $C_2-C_3$ ,  $C_3-H_3$ ) and two types of bond angles ( $C_2-N_1=N'_1$ ,  $N_1-C_2-C_3$ ) were refined independently. The remaining distances C-C and C-H were tied to the appropriate parameters mentioned above by the difference between the nonequivalent structural parameters of the same type. Angles C-C-C were tied to the angle  $N_1-C_2-C_3$ . The amplitudes were refined in five groups corresponding to the different peaks on the radial distribution curve.

The RM imposes softer constraints. Compared to Equation (2) for the MOCED method, a penalty functional  $\alpha_{reg} \cdot \Phi_{QC}(\alpha_{reg})$  based on the computed quantum chemical parameter has been added to the equation of refinement in the framework of RM. The second term in Equation (3) essentially restricts the  $k$ -th parameter to some limits determined by the  $\alpha_{reg}$  coefficient. Thus, a choice of the  $\alpha_{reg}$  value is decisive in the framework of this refinement approach. Under this investigation for different starting sets of internuclear distances,

vibrational amplitudes and corrections, the regularization constants  $\alpha_{reg}$  were adjusted as a minimum for Equation (4) [80].

$$\ln^2 \left( \frac{\sum_i \Phi_{GED}(\alpha_{reg})}{\alpha_{reg} \cdot \sum_k w_k (p_k^0 - p_k)^2 (\alpha_{reg})} \right) \rightarrow \min \quad (4)$$

In a least squares (LS) analysis, the disagreement factor  $R_f$  between experimental and theoretical scattering intensity was calculated as

$$R_f = \sqrt{\frac{\sum_{i=1}^N (s_i M(s_i)^{exp} - k_M s_i M(s_i)^{theor})^2}{\sum_{i=1}^N (s_i M(s_i)^{exp})^2}} \cdot 100\% \quad (5)$$

where  $s_i M(s_i)^{theor}$ —theoretical molecular scattering intensities;  $s_i M(s_i)^{exp}$ —experimental molecular scattering intensities from [30]; and  $k_M$ —the scale factor.

The weights of the parameters in (3) were obtained ( $w_k = \sigma_k^{-2}$ ) from their ascribed standard deviations ( $\sigma_k$ ): 0.005 Å for bond lengths (0.01 Å for hydrogen bonds) and 0.5° for valence and dihedral angles. Contributions of the terms of Equation (2) to the refined parameters were estimated using the W2 method described in ref. [81].

In this work, structural analysis was carried out using: (i) a semirigid (static) model [31,82]; (ii) one-dimensional dynamic models constructed using pseudoconformers and potential energy function [31,82,83]; and (iii) a two-dimensional pseudoconformer model constructed using a mixture of molecules [29].

### 2.2.2. One-Dimensional Dynamic Models

We have carried out a one-dimensional dynamic version of GED data processing in three variants: (DM1) pseudoconformers obtained by rotation of only one phenyl group were considered (similar to the original work [30]); (DM2) pseudoconformers belonging to the  $C_2$  point group of symmetry, obtained by synchronous rotations of two phenyl groups or rotational vibration of  $A_u$  symmetry, were considered; and (DM3) pseudoconformers belonging to the point group of symmetry  $C_i$ , obtained by synchronous rotations of two phenyl groups or vibration of  $B_g$  symmetry, were considered. The fully relaxed scan of the  $\varphi = 0^\circ$ – $90^\circ$  coordinates at intervals of  $15^\circ$  and appropriate calculations of harmonic frequencies of vibrations at the B3LYP-D3/pcseg-2 level were carried out. The potential function was approximated by Equation (6), consistent with the need for the function to be symmetrical with respect to  $\varphi = 0$  and  $\pi/2$ :

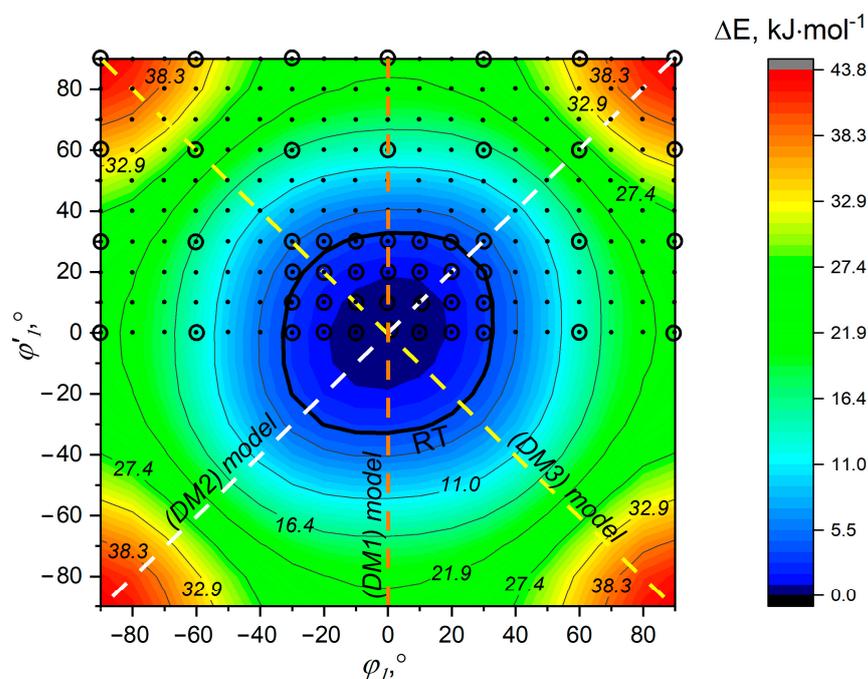
$$V = V_0 + V_2(1 - \cos(2\varphi)) + V_4(1 - \cos(4\varphi)) \quad (6)$$

Abundances of the pseudoconformers were calculated using relative energies of structures and Boltzmann distribution. Vibrational amplitude  $l$  and vibrational corrections  $r_{h1} - r_a$  were computed using the VibModule program from quadratic force fields with the exception of (i) in the case of (DM1) and (DM2) variants—the vibrational mode corresponding to lowest mode of  $A_u$  symmetry under  $C_{2h}$  point group—and (ii) in case of (DM3) variant—the vibrational mode corresponding to lowest mode belonging to the  $B_g$  irreducible representation under  $C_{2h}$  point group.

### 2.2.3. 2D Pseudoconformer Model

The 2D pseudoconformer model was based on 190 rotational pseudoconformers with  $\varphi_1 \in [-90^\circ; 90^\circ]$  and  $\varphi'_1 \in [0^\circ; 90^\circ]$  with a step of  $\Delta\varphi = 10^\circ$  (Figure 2). Due to the fact that the remaining part of the PES is symmetrical to the considered region, the remaining structures were not considered separately but were taken into account by correspondingly changing values for mole fractions. Abundances of the pseudoconformers were calculated using Boltzmann distribution on the basis of B3LYP-D3/pcseg-2 relaxed scan calculations

and were fixed in the structural refinement. Vibrational amplitude 1 and vibrational corrections  $r_{h1} - r_a$  for pseudoconformers marked in Figure 2 with circles were computed from quadratic force fields with the exclusion of two vibrational modes corresponding to phenyl rotations. For the remaining structures (correspond to the points in Figure 2), the corresponding parameters were calculated using the force field of the nearest structure, for which the harmonic vibration frequencies were calculated (corresponding to the circles in Figure 2).



**Figure 2.** PES obtained at the B3LYP-D3/pcseg-2 level of theory as a function of rotations of two phenyl moieties around N-C bonds. Bold line RT corresponds to the temperature of GED experiment ( $T_{\text{exp}} = 407$  K) [30]. The points correspond to the structures taken into account in the 2D pseudoconformer model. Circles mark structures for which harmonic frequencies were calculated for subsequent evaluation of vibrational amplitudes and corrections for 2D pseudoconformer model analysis. The dashed lines indicate geometries on the PES that are actually described by the structural analyses using dynamic models.

### 3. Results and Discussion

#### 3.1. Multireference Nature of the Electronic Wave Function

In order to determine the multireference nature of the electronic wave function, an analysis of well-known diagnostic parameters (the Euclidean norm of the vector of  $t_1$  amplitudes or  $T_1$  [84], value of the largest double excitation amplitudes or  $T_2$  [85,86],  $N_{\text{FOD}}$ ) was carried out. It is noted that to apply a single-reference approach to describe a system,  $T_1$  and  $T_2$  values should not exceed 0.02 [84] and 0.1–0.2 [87]. The  $T_1$  (0.011 for both isomers) and  $T_2$  (0.046—for E-, 0.063—for Z-isomers) values were also within acceptable limits for the use of single-reference methods. FOD are largely localized on the nitrogen atoms (Figure S1). FOD diagnostic provides values of 0.344 and 0.299 for E- and Z-isomers, respectively. These indicators can be compared with data on nitroxoline and anthracene molecules ( $N_{\text{FOD}} = 0.215$  and 0.249), for which the applicability of single-reference methods was previously justified [88].

#### 3.2. Evaluation of Optimized Geometries

MP2/6-31+G\* predicted a twisted structure of E-AB [30]. DLPNO-CCSD(T0)/CBS // MP2/6-31+G\* calculations indicate that the planar structure is energetically advantageous by  $1.4 \text{ kJ}\cdot\text{mol}^{-1}$ . According to all DFT calculations mentioned in Section 2, as expected,

E-AB has a flat structure of  $C_{2h}$  symmetry. It is worth noting that the M05 calculation gave one imaginary frequency for the structure of  $C_{2h}$  symmetry and the minimum turned out to be very close to it. However, by increasing the grid size, this problem was solved: all frequencies for the  $C_{2h}$  symmetry structure are real.

QC calculations predict the structural parameters of E-AB with large uncertainty. Internuclear distances from DFT/pcseg-2 calculations are lower than those obtained [30] in MP2/6-31+G\*. The use of different DFT functionals leads to quite strong differences in geometry (Table S2), primarily in the value of the N=N bond length from 1.221 Å (M06HF) to 1.267 Å (BP86). In this study, the quality of different DFT geometries is evaluated by calculating the DLPNO-CCSD(T0)/CBS energies for all optimized structures in a similar manner as the authors of ref. [63]. The lowest-energy (DLPNO-CCSD(T0)) structure is provided by the BMK functional (Table S3). Energy differences within 0.5 kJ·mol<sup>-1</sup> were derived for structures optimized by B3LYP, B98, and TPSSh calculations. More than 3.0 kJ·mol<sup>-1</sup> higher energy corresponds to the structures obtained by the LC-wPBE and M06HF (underestimating internuclear distances compared to BMK results), BP86, and PBE (overestimating internuclear distances compared to BMK results) functionals. Similar results were achieved within the framework of the analysis of optimized geometries of Z-AB (Table S4).

### 3.3. E-AB vs. Z-AB: Capabilities of GED Method

E-AB is energetically much more preferable compared to Z-AB. According to the DFT calculations considered, the gain in energy of the E-AB ranges from 43 to 63 kJ·mol<sup>-1</sup>, while higher-level DLPNO-CCSD(T0)/CBS calculations predict this value to be ca. 51 kJ·mol<sup>-1</sup> (Table S5). The E-AB→Z-AB transition significantly affects the N<sub>1</sub>-C<sub>2</sub> and N<sub>1</sub>-N'<sub>1</sub> bond lengths: the difference in the values of these parameters in the two isomers are ca. 0.01 and ca. 0.02 Å, respectively [20]. The simulated radial distribution curves  $f(r)$  for E-AB and Z-AB differ significantly (Figure S2). Therefore, it is possible to distinguish cis- and trans-isomers of azobenzene and its derivatives. The structural analysis carried out in this work with assumptions of the cis-structure of AB poorly describes the experimental data presented in the work [30]. Modeling mixtures of trans- and cis-isomers in structural analysis also indicates the absence of Z-AB in the vapors under experimental conditions.

### 3.4. Does the Quality of Starting Parameters for GED Analysis Strongly Depend on the Choice of DFT Functional?

In GED structural refinement, three groups of parameters derived from theoretical calculations are used: internuclear distances, vibrational amplitudes, and corrections to internuclear distances. The first two groups usually vary during the LS procedure. In order to determine the spread of the starting parameters obtained by different QC calculations, the relative ranges R determined by Equations (7) and (8) were used for analysis.

$$R(p) = \frac{p_{max} - p_{min}}{\langle r_e \rangle} \times 100\% \quad (7)$$

where p is one of the parameters for pairs of atoms X<sub>i</sub> and Y<sub>j</sub> (X<sub>i</sub>, Y<sub>j</sub> = H, C, N): (i) internuclear distances  $r_e$ ; (ii) differences between internuclear distances  $\Delta r_e$  equal to  $r_e(C_1-C_j) - r_e(C_2-C_3)$  or  $r_e(C_1-C_j) - r_e(N_1-C_2)$  or  $r_e(X_i-X_j) - r_e(N_1=N'_1)$ ;  $p_{max}$  and  $p_{min}$  are maximal and minimal values of the parameter p among those found by considered QC calculations; and  $\langle r_e \rangle$  is the average value of the internuclear distance  $r_e$  for term X<sub>i</sub>-X<sub>j</sub> according to calculations using various functionals. Since the internuclear distances from the BMK calculations turned out to be approximately average among their analogues obtained in the considered set of calculations, we can use  $r_e(\text{BMK})$  instead of the  $\langle r_e \rangle$  in Formula (7). Thus, to analyze the ranges of vibrational amplitudes and vibrational corrections, Equation (8) was used.

$$R(p) = \frac{p_{max} - p_{min}}{r_e(\text{BMK})} \times 100\% \quad (8)$$

where  $p$  is one of the parameters for pairs of atom  $X_i$  and  $Y_j$  ( $X_i, Y_j = \text{H, C, N}$ ): vibrational amplitudes  $l$ , vibrational corrections ( $r_e - r_a$ ) or ( $r_{h1} - r_a$ );  $p_{max}$  and  $p_{min}$  are maximal and minimal values of the parameter  $p$  among those found by QC calculations; and  $r_e(\text{BMK})$  is the value of internuclear distance  $r_e$  by BMK calculations.

### 3.4.1. Internuclear Distances

Within the framework of the widely used MOCED method [32], in order to reduce the correlation between the independent parameters and improve the stability of the LS procedure, internuclear distances are combined into groups by the constraining differences (in general,  $\Delta r = r(X_i - X_j) - r(X_m - X_n)$ ) between them within each group. In this case, obviously false differences taken from the theory will spoil GED structural refinement. It is worth mentioning that this problem can be solved by using the regularization procedure [77–79] but then it is necessary to decide the issue of choosing a suitable regularization factor  $\alpha_{reg}$  as carried out in this work by using Equation (4), or in other possible ways [89].

Previously, researchers [30] used four groups of bonded atom pairs: N=N, N-C, C-C, and C-H, despite the fact that a significant correlation ( $-0.79$ ) was observed between the groups N-C and C-C. In this approach, differences between internuclear distances  $\Delta r_e$  should be kept only for terms C-C (i.e.,  $\Delta r_e(C_i - C_j) = r_e(C_i - C_j) - r_e(C_2 - C_3)$ ). The maximum spread in the  $\Delta r_e$  parameters equal to  $\Delta r_e = 0.012 \text{ \AA}$  ( $\Delta r_{min} = \Delta r_{B97D} = -0.015 \text{ \AA}$ ,  $\Delta r_{max} = \Delta r_{M06HF} = -0.003 \text{ \AA}$ ) was found for the distance C<sub>6</sub>-C<sub>7</sub>. This deviation corresponds to  $R(\Delta r) = 0.8\%$  of the internuclear distance. When combining groups C-C and N-C, the maximum spread in the  $\Delta r$  will already be  $0.033 \text{ \AA}$ , which corresponds to  $R(\Delta r) = 2.4\%$  (Table S1). In the case of a rough constraining of all distances of the molecular framework (combining groups N=N, N-C and C-C), the maximum spread in the  $\Delta r$  becomes equal to  $0.056 \text{ \AA}$  (or  $R(\Delta r) = 4\%$ , Table S1). This can lead to optimization problems within the framework of structural analysis. For AB, the variant of dividing all bonding distances into four groups is justified based on the data presented and was used in current work for all MOCED refinements.

### 3.4.2. Vibrational Amplitudes

LC-wPBE calculations predict a shallow potential function of E-AB along the N=N-C-C torsional coordinates and a low vibrational frequency,  $\omega_{rot.Ph} = 6.6 \text{ cm}^{-1}$ , corresponding to the rotation of the phenyl rings (Table S6). A quite low frequency ( $\omega_{rot.Ph} < 13 \text{ cm}^{-1}$ ) is also obtained in the calculations using M05 and M06HF functionals. This results in overestimated vibrational amplitudes and corrections that are very different from those obtained on the base of all other calculations. When comparing the acquired amplitude values for all remaining calculations (13 functionals), it can be noted that the average spread in the vibrational amplitudes is  $R(l)_{ave} = 0.39\%$  (Figure S3). The average relative range in vibrational corrections is  $r_{h1} - r_a$  is  $0.65\%$  (Figure S4). The maximal ranges in vibrational amplitudes (corrections) were found only for six (twenty four) unbonded distances  $X \cdots H_{3,7,3',7'}$ :  $R(l) = 2\text{--}5\%$  ( $R(r_{h1} - r_a) = 2\text{--}8\%$ ) (Figures S3 and S4). Due to the poor determination of the position of hydrogen atoms in the GED method, these differences in the predicted parameters should not play a large role in the convergence of the LS procedure and the resulting final semiexperimental structure. The spread of the obtained vibrational corrections ( $r_e - r_a$ ) and ( $r_{h1} - r_a$ ) is similar (Figures S4 and S5). Ignoring the first low frequency when calculating vibrational amplitudes and corrections leads to very similar values ( $R(l)_{ave} = 0.19\%$ ,  $R(r_{h1} - r_a)_{ave} = 0.22\%$ ), regardless of the functional used in QC calculations (even in the case of functionals LC-wPBE, M05 and M06HF) (Figures S6 and S7). Such vibrational parameters are suitable for use in a dynamic model.

Next, we checked how significant the found ranges in the values of the starting parameters would be for the LS analysis. LS procedures carried out within the framework of the MOCED method gave results that were in good agreement with each other and with the results of the work [30]. In almost all cases, it was possible to achieve both a low disagreement factor,  $R_f$ , and the same semiexperimental structural parameters of the

molecule. The exceptions were analyses that used overestimated starting parameters taken from LC-wPBE, M05, and M06HF calculations (Tables S7 and S8, Figures S8 and S9). Thus, we can note the relatively good stability of the structural analysis to the choice of starting values of internuclear distances, vibrational amplitudes, and corrections.

In the case of structural analysis using the regularization method, one of the important fundamental actions is the choice of  $\alpha_{reg}$ . In this work,  $\alpha_{reg}$  was chosen separately for each set of starting values used in LS analysis. However, this approach showed less stability than within the MOCED method. RM still gives some ranges in the resulting disagreement factors,  $R_f$ , and, accordingly, in the structural parameters  $r_g$  (Tables S9 and S10, Figures S10 and S11). With all this, the structures corresponding to an acceptably low  $R_f$  are very close to each other. It is also worth noting the stability of the structural analysis when changing the harmonic field to a cubic one: the structural parameters in terms of  $r_g$  within the error limits are in good agreement (Tables S7–S10).

### 3.5. GED Analysis: Semirigid, One-Dimensional Dynamic and Two-Dimensional Dynamic Models

The rotational vibration of  $A_u$  symmetry (symmetrical relative to the  $C_2$  axis) of the phenyl rings has a low frequency  $\sim 17\text{ cm}^{-1}$  (Table S6). According to the DLPNO-CCSD(T0)/CBS // B3LYP-D3/pcseg-2 calculation, the rotation barrier of one phenyl group is estimated to be about  $19\text{ kJ}\cdot\text{mol}^{-1}$ . Within the framework of the simultaneous rotation of two phenyl rings (along the  $\tau(N_1=N'_1-C'_2-C'_3) + \tau(N_1=N'_1-C'_2-C'_7) + \tau(N'_1=N_1-C_2-C_3) + \tau(N'_1=N_1-C_2-C_7)$  torsional coordinate), the barrier becomes equal to ca.  $37\text{ kJ}\cdot\text{mol}^{-1}$  (Figure S12). It is important to note that different DFT calculations yield a large range in the barrier value—from 32 (LC-wPBE) to  $72\text{ kJ}\cdot\text{mol}^{-1}$  (VSXC). The rotation of the phenyl rings is accompanied by the breaking of the  $\pi$  conjugation and the corresponding lengthening of the N-C bonds and shortening of the  $N_1-N'_1$  bond (Figure S13). However, in the extensive area near the minimum in the PES of E-AB (at least with  $-30^\circ < \varphi < 30^\circ$ ), the geometric changes are insignificant (Figure S13) and do not lead to a strong increase in the relative energy (Figures 2 and S12). Based on the softness of potential along the phenyl rotation vibration coordinate, it is indeed justified to consider these rotations as large-amplitude motions and using dynamic a GED model in structural analysis.

It turned out that in dynamic GED analysis, the refined values of the parameters  $V_0$ ,  $V_2$ ,  $V_4$  from Equation (4) had large standard deviations and were unreliable. Therefore, it was decided to fix the parameters of the potential function in the structural refinement. All three structural analyses using different dynamic models DM1, DM2, and DM3 give almost identical structural parameters of the molecule and the values of  $R_f$  equal to 3.5–3.6%. However, these approaches to accounting for large-amplitude motions are also limited in that they describe the PES profile in Figure 2 under restrictions marked by dashed lines only. To eliminate this shortcoming, a structural analysis in the framework of a 2D pseudoconformer model can be performed, as recommended in the work for stilbene [29]. According to this consideration, the same structure of E-AB was obtained as in the case of previous analyses but with a slightly larger disagreement factor  $R_f = 3.7\%$ .

In the next step, a structural analysis using a static model was performed. A semirigid model agreed well with experimental data giving  $R_f = 3.5\%$ . The smaller  $R_f$  in the case of the semirigid model should not come as a surprise. Previously, the authors of ref. [90] studying the diaziridine derivative explained similar results due to two reasons: (i) dynamic models required a large number of not-refined constraints taken from theoretical calculations; and (ii) the fallacy of the theoretical potential used.

Additionally, we checked the possibility of determining the torsion angles  $\varphi_1$  and  $\varphi'_1$  using a semirigid model, for which we carried out (i) a comparison of the theoretical radial distribution curves  $f(r)$  for pseudoconformers, discussed above in the study of individual phenyl moiety rotation and synchronous rotations of two phenyl groups; and (ii) least-squares analyses for pseudoconformers using a static model with freezing dihedral angle values  $\varphi_1$  and  $\varphi'_1$ . Models of considered pseudoconformers with  $0^\circ < |\varphi_1; \varphi'_1| < 30^\circ$

should equally describe the experimental data, as indicated by minor differences in the theoretical radial distribution curves  $f(r)$  and the corresponding small values of  $R_f^{theor}$  (Figures S14–S16). An analysis of the experimental data using the planar structure of  $C_{2h}$  symmetry and pseudoconformers with rotation angles  $\varphi$  up to  $\sim 30^\circ$  as a starting approximation makes it possible to obtain almost the same disagreement factors,  $R_f \approx 3.5\%$  (Figure S17). Using Hamilton's criterion [91] shows that the uncertainty in determining the angle  $\varphi$  is about  $40^\circ$ . This value agrees well with the results of the DLPNO/CCSD(T0) calculated potential energy: the thermal energy,  $RT_{exp}$ , corresponds to the relative energy of the conformer with  $\varphi_1 = 37^\circ$  and  $\varphi'_1 = 0^\circ$ .

### 3.6. Semiexperimental Equilibrium Structure

A structural analysis within the framework of dynamic and 2D pseudoconformer models provide similar structural parameters and disagreement factors  $R_f$  as the refinement using a semirigid model. Based on the results of this work, the structure refined from the B3LYP-D3/pcseg-2 calculated a geometry within the MOCED method using a semirigid model was chosen as the final semiexperimental equilibrium structure (Tables 1 and S11).

**Table 1.** Structural parameters <sup>a</sup> of E-AB according to QC <sup>b</sup> and GED.

	B3LYP-D3/ /pcseg-2	GED Our Refinement <sup>c</sup> , Experimental Data from Ref. [30]		GED Refinement and Experimental Data from Ref. [30]	GED Refinement and Experimental Data from Ref. [28]	
	$r_e$	$r_e^d$	$r_g^e$	$r_g^f$	$C_2$ $r_g^f$	$C_i$ $r_g^f$
N <sub>1</sub> =N' <sub>1</sub>	1.248	1.255(8)	1.260(9)	1.260(8)	1.261(12)	1.270(12)
N <sub>1</sub> -C <sub>2</sub>	1.417	1.417(9)	1.427(10)	1.427(8)	1.423(12)	1.430(12)
C <sub>2</sub> -C <sub>3</sub>	1.400	1.397(3)	1.403(2)	1.405(1)	-	-
C <sub>2</sub> -C <sub>7</sub>	1.395	1.393(3)	1.401(2)	1.401(1)	-	-
C <sub>3</sub> -C <sub>4</sub>	1.384	1.382(3)	1.392(2)	1.393(1)	-	-
C <sub>6</sub> -C <sub>7</sub>	1.389	1.386(3)	1.393(2)	1.396(1)	-	-
C <sub>4</sub> -C <sub>5</sub>	1.395	1.392(3)	1.399(2)	1.402(1)	-	-
C <sub>5</sub> -C <sub>6</sub>	1.390	1.387(3)	1.397(2)	1.397(1)	-	-
C-C av	1.394	1.391(3)	1.398(2)	1.399(1)	1.398(3)	1.398(3)
C-H av	1.081	1.076(7)	1.098(8)	1.102(7)	1.087(9)	1.093(9)
N' <sub>1</sub> =N <sub>1</sub> -C <sub>2</sub>	115.6	114.2(9)	114.2(9)	113.6(8)	116.0(12)	114.5(12)

<sup>a</sup> bond distances in Å, valence angle—in °. <sup>b</sup> internuclear distances from different DFT calculations are given in the Table S2. <sup>c</sup> MOCED, semirigid model, cubic force fields from B3LYP-D3/pcseg-2 calculations were used to generate the starting internuclear distances, vibration amplitudes, and corrections ( $r_e - r_a$ ). <sup>d</sup> uncertainties for the bond lengths were estimated as  $[(2.5\sigma_{LS})^2 + (0.002r)^2]^{1/2}$ ; uncertainty for the angle was estimated as  $3\sigma_{LS}$ . <sup>e</sup> uncertainties were estimated as  $3\sigma_{LS}$ . Here, an another method for calculating uncertainties was chosen in order to provide a more adequate comparison with the results presented in [30], where this particular formula was used. <sup>f</sup> uncertainties were estimated as  $3\sigma_{LS}$ .

Comparing the results of the GED structural analyses obtained by us (using the experimental data of [30]) and by the authors of refs. [28,30], it can be concluded that the internuclear distances in terms of  $r_g$  are in good agreement with each other within the experimental error (Table 1). If the work in ref. [30] concluded that E-AB was planar, then the older work in ref. [28] stated that the molecules have distorted conformations with the phenyl groups twisted approximately  $30^\circ$  around the N-C bonds. Moreover, as reported by the authors of ref. [28], it was not possible to decide whether the phenyl groups were rotated to the same or to the opposite side relative to the azo bridge. Numerous variants of structural analysis carried out in this work indicate that the GED experiment unreliably determines the torsion angles  $\varphi_1$  and  $\varphi'_1$  as well as parameters  $V_i$  of potential function. This can be attributed to the facts that (i) flat and twisted (with  $0^\circ < |\varphi_1; \varphi'_1| < 30^\circ$ ) structures have internuclear distances close to each other; and (ii) the PES of E-AB is shallow along the N=N-C-C torsional coordinates. However, accompanied by high-level QC calculations, it can be stated that equilibrium structure of E-AB is planar. In this work, we also defined for the first time the GED structure of E-AB in terms of the  $r_e$  parameters that we recommend for terminologically correct comparison with QC optimized structural parameters for AB and its derivatives.

#### 4. Conclusions

The AB considered in the work is the parent compound of many practically important compounds. It serves as a reference point in the search for new substances and materials, promising for practical application and for prediction of their physicochemical properties. The special importance is the knowledge about accurate molecular structure since it is the basis for all stereochemical constructions.

The semiexperimental equilibrium structure of the E-AB molecule was obtained and can be recommended as the most accurate to date. We can conclude that, according to the GED experiment, E-AB has a planar structure. High-level DLPNO-CCSD(T0) calculations confirmed that the flat geometry corresponds to the minimum on the PES. It is shown that, despite some nonrigidity of the E-AB molecule, the structural analysis using a dynamic model and an even more expensive 2D model is redundant. These variants of structural analyses did not lead to any noticeable decrease in the disagreement factor  $R_f$  compared to using the semirigid model. The resulting structural parameters of the planar pseudoconformer are almost identical according to these refinements. Determination of the experimental potential along the rotation coordinate of phenyl fragments using a dynamic model is associated with high errors in the coefficients  $V_i$ , which actually indicates the impossibility of this determination by means of GED. Rotation of the phenyl rings around the N-C bond at  $\varphi \approx -40^\circ \div 40^\circ$  is probable under the experimental conditions but does not lead to significant changes in the bonded distances in the molecule. It is also noted that the relative energy of the Z-AB isomer is much greater than the thermal energy  $RT_{\text{exp}}$ , so there is no need to consider the cis isomer as a component of the vapor under the experiment. These conclusions are recommended to be used to simplify the nontrivial structural analysis of the conformationally more complex azobenzene derivatives.

The influence of the DFT functional choice for the prediction starting parameters (distances, amplitudes, corrections) on the GED structural analysis results was considered. Despite the good agreement between the energetic parameters (the barriers of phenyl rotations, the relative energies of the Z- and E- isomers) obtained using LC-wPBE, M05, and M06 calculations with higher-level data of DLPNO-CCSD(T0), molecular structures and vibrational parameters ( $l$ ,  $r_e - r_a$ ,  $r_{h1} - r_a$ ) from the LC-wPBE, M05, and M06 results turned out to be unsuitable for refinement using a semirigid model. The remaining DFT calculations generally performed well in structural analysis. Despite the above, M05 predicted a structure that is in good agreement with the GED results. B3LYP, mPW1PW91, PBE0, TPSSh, and X3LYP calculations also predict the structure to within the error of a GED experiment, while GGA calculations (B97D, BP86, and PBE) overestimate NN and CC distances. Based on a comparison with the results of the GED experiment and the results of high-level DLPNO-CCSD(T0) calculations, it can be recommended to use the B3LYP, TPSSh, and X3LYP functionals for studying the molecular structure of azobenzene derivatives.

**Supplementary Materials:** The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/physchem4020010/s1>, Figure S1: FOD plot for AB; Figure S2: Comparison of theoretical radial distribution functions  $f(r)$  of E-AB and Z-AB; Figure S3: Relative ranges of vibrational amplitudes  $R(l)$  for pairs of atom  $X_i$  and  $Y_j$  ( $X_i, Y_j = \text{H, C, N}$ ); Figure S4: Relative ranges of vibrational corrections  $R(r_{h1} - r_a)$  for pairs of atom  $X_i$  and  $Y_j$  ( $X_i, Y_j = \text{H, C, N}$ ); Figure S5: Relative ranges of vibrational corrections  $R(r_e - r_a)$  for pairs of atom  $X_i$  and  $Y_j$  ( $X_i, Y_j = \text{H, C, N}$ ); Figure S6: Relative ranges of vibrational amplitudes  $R(l)$  for pairs of atom  $X_i$  and  $Y_j$  ( $X_i, Y_j = \text{H, C, N}$ ); Figure S7: Relative ranges of vibrational corrections  $R(r_{h1} - r_a)$  for pairs of atom  $X_i$  and  $Y_j$  ( $X_i, Y_j = \text{H, C, N}$ ); Figure S8: Results of GED structural refinement for E-AB in the framework of MOCED method using starting parameters  $r_e, l, r_{h1} - r_a$  obtained by different DFT calculations; Figure S9: Results of GED structural refinement for E-AB in the framework of MOCED method using starting parameters  $r_e, l, r_e - r_a$  obtained by different DFT calculations; Figure S10: Results of GED structural refinement for E-AB in the framework of RM using starting parameters  $r_e, l, r_{h1} - r_a$  obtained by different DFT calculations; Figure S11: Results of GED structural refinement for E-AB in the framework of RM using starting parameters  $r_e, l, r_e - r_a$  obtained by different DFT calculations; Figure S12: Potential energy function of simultaneous rotation of two phenyl rings around the

N<sub>1</sub>-C<sub>2</sub> and N'<sub>1</sub>-C'<sub>2</sub> bonds in the E-AB molecule, calculated in different approximations; Figure S13. Internuclear distances N<sub>1</sub>-N'<sub>1</sub> (red circles) and N<sub>1</sub>-C<sub>2</sub> (blue squares) vs. dihedral angles  $\varphi_1$  and  $\varphi'_1$  in the E-AB molecule from the B3LYP-GD3/pcseg-2 calculations; Figures S14–S16: Comparison of theoretical radial distribution functions  $f(r)$  of pseudoconformers of E-AB; Figure S17: The ratio of disagreement factors  $R_f$  as a function of torsion angles  $\varphi_1$  and  $\varphi'_1$ , responsible for rotation of phenyls; Table S1. Unex Z-matrix of E-AB; Table S2: Structural parameters (Å) of E-AB according different DFT-calculations; Table S3: Relative energies of E-AB according DLPNO-CCSD(T0) calculations; Table S4: Relative energies of Z-AB according DLPNO-CCSD(T0) calculations; Table S5: Energies of Z-AB relative to the E-AB according DLPNO-CCSD(T0) calculations; Table S6: Relative energies of pseudoconformers of E-AB and vibrational frequency of phenyls rotations according DFT, MP2 and DLPNO-CCSD(T0) calculations; Table S7: Internuclear distances  $r_g$  of E-AB determined by MOCED structural analyzes using starting internuclear distances  $r_e$ , vibrational amplitudes  $l$  and corrections  $r_e - r_a$  from results of different DFT calculations; Table S8: Internuclear distances  $r_g$  of E-AB determined by MOCED structural analyzes using starting internuclear distances  $r_e$ , vibrational amplitudes  $l$  and corrections  $r_{h1} - r_a$  from results of different DFT calculations; Table S9: Internuclear distances  $r_g$  and corresponding contribution of experimental GED data to parameters ( $w$ ) of E-AB determined by RM structural analyzes using starting internuclear distances  $r_e$ , vibrational amplitudes  $l$  and corrections  $r_e - r_a$  from results of different DFT calculations. Table S10: Internuclear distances  $r_g$  and corresponding contribution of experimental GED data to parameters ( $w$ ) of E-AB determined by RM structural analyzes using starting internuclear distances  $r_e$ , vibrational amplitudes  $l$  and corrections  $r_{h1} - r_a$  from results of different DFT calculations; Table S11: Cartesian atomic coordinates of final semiexperimental equilibrium structure ( $r_e$ ) of E-AB according GED method.

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