# Cis–Trans Isomerization about the Carbon–Nitrogen Double Bond. The Structures of the Isomers of *N*-Benzylideneaniline

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**Abstract:** CNDO molecular orbital calculations for *N*-benzylideneaniline (NBA) predict, in agreement with experimental observations, that two stable configurations of this molecule exist. Minimum-energy conformations of the trans and cis forms with respect to three relevant degrees of freedom [C=N—$C_6H_5$ angle ($\phi$), rotation angles N—$C_6H_5$ ($\theta$) and C—$C_6H_5$ ($\gamma$)] have been determined. In both cases they are *nonplanar*, having $\phi = 117°$, $\theta = 90°$, and $\gamma = 53°$ for *trans*-NBA and $\phi = 253°$, $\theta = \gamma = 90°$ for *cis*-NBA. For the trans isomer, the C–$C_6H_5$ ring has essentially free rotation (barrier *ca.* 0.4 kcal/mol), whereas for the N–$C_6H_5$ ring the rotation barrier is *ca.* 7 kcal/mol. The calculations indicate that interconversion of the isomers occurs by inversion at the nitrogen atom rather than by rotation about the C–N double bond. The energy barrier for cis–trans isomerization by inversion is estimated to be 21.2 kcal/mol, which compares favorably with the experimental activation energy of 16.5 kcal/mol.

There is currently considerable interest in isomerization about the C=N double bond, a topic which has recently been reviewed.[2] *N*-Benzylideneaniline (NBA), Figure 1, in which two aromatic rings are linked by a C=N bridge, is representative of compounds which can apparently undergo cis–trans isomerization. The stable form of this molecule, which has just been established to have a trans configuration in the crystalline state,[3] can be photochemically converted into an unstable form which is believed to have the cis configuration.[4,5]

The ultraviolet spectrum of NBA is remarkably different from that of the isoelectronic molecules azobenzene (N=N linkage) and stilbene (C=C linkage). The anomalous spectrum of NBA has prompted several theoretical investigations of the electronic and geometrical structure of this molecule. Minkin and coworkers,[6,7] and Favini and Gamba,[8] using simple Hückel molecular orbital (HMO) theory, deduced that the phenyl ring attached to the nitrogen atom (ring A, Figure 1) is rotated out of plane with respect to the rest of the molecule. More recently, Houlden and Csizmadia[9] applied the extended HMO theory to NBA. These authors assumed a *planar* structure for NBA, and calculated the energy as a function of the $C_6H_5$—C=N and $C_6H_5$—N=C angles. The latter angle was concluded to be unusually large (156°), and the barrier to the formation of the cis isomer was estimated to be only *ca.* 4 kcal/mol, which is smaller than the expected value by a factor of at least 4. Moreover, the agreement between the calculated and the observed transition energies was not satisfactory; this finding is not surprising in view of the basic assumptions of extended HMO theory.

Although the experimental evidence suggests that the interesting chemical and physical properties of NBA stem from its nonplanarity, there is still controversy regarding the detailed structure of this molecule in the free state. In the crystalline state, NBA had recently been shown to be nonplanar.[3]

In this paper, we report the application of the CNDO method[10–13] to the study of the properties of NBA. This method is particularly suited to molecules with nonplanar conformations since it is based on an SCF treatment of all valence electrons. The specific objectives of this study were to (1) establish the ground-state conformation of the trans and cis isomers of NBA, and (2) to provide information about the mechanism and energetics of their interconversion. The spectral properties of the NBA isomers will be considered in a forthcoming publication.

## Method of Calculation

For the calculation of the ground-state properties of NBA, the CNDO/2 method[12] was adopted without modification. The parameters used were those developed by Pople and Segal.[11,12] In this form, the method has been successfully applied to many structural problems involving small molecules.

Since NBA has a large number of internal degrees of freedom, it was not feasible to simultaneously minimize the energy with respect to all of them. We therefore chose to focus our attention on those degrees of freedom which intuition tells us are likely to be most important, *i.e.*, the rotations of rings A and B with respect to the C—C=N—C plane (angles $\theta$ and $\gamma$, respectively), the variation of the C=N—$C_6H_5$ angle ($\phi$), and rotation about

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(2) G. Wettermark, *Sv. Kem. Tidskr.*, 79, 249 (1967); G. Wettermark in "The Chemistry of Functional Groups," Vol. 3, S. Patai, Ed., Wiley, London, 1969, p 565.

(3) H. B. Bürgi and J. D. Dunitz, *Chem. Commun.*, 472 (1969).

(4) E. Fischer and Y. Frei, *J. Chem. Phys.*, 27, 808 (1957).

(5) D. G. Anderson and G. Wettermark, *J. Amer. Chem. Soc.*, 87, 1433 (1965).

(6) V. I. Minkin, E. A. Medyantzeva, and A. M. Simonov, *Dokl. Akad. Nauk SSSR*, 149, 1347 (1963).

(7) V. I. Minkin, Y. A. Zhodanov, E. A. Medyantzeva, and Y. A. Ostroumov, *Tetrahedron*, 23, 3651 (1967).

(8) G. Favini and A. Gamba, *J. Chim. Phys. Physicochim. Biol.*, 62, 995 (1965).

(9) S. A. Houlden and I. G. Csizmadia, *Tetrahedron*, 25, 1137 (1969).

(10) J. A. Pople, D. P. Santry, and G. A. Segal, *J. Chem. Phys.*, 43, S129 (1965).

(11) J. A. Pople and G. A. Segal, *ibid.*, 43, S136 (1965).

(12) J. A. Pople and G. A. Segal, *ibid.*, 44, 3289 (1966).

(13) D. P. Santry and G. A. Segal, *ibid.*, 47, 158 (1967).

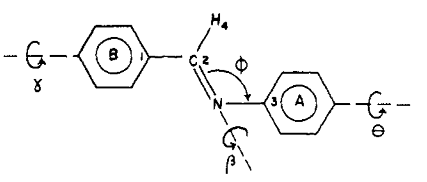

Figure 1. Gross structure of *N*-benzylideneaniline (NBA).

the C—N double bond (angle β). All the other bond angles and bond distances were assumed to be constant. When these calculations were initiated, the geometry of NBA was not known. Therefore, an average geometry based on the known structures of several disubstituted *N*-benzylideneanilines[14] was used to obtain the bond distances and angles for a hypothetical planar conformation of NBA. The average parameters for this planar configuration are listed in Table I.

**Table I.** Bond Distances and Angles Assumed for Planar *trans*-NBA

| Bond | Distance, Å | Angle | Size, deg |
|---|---|---|---|
| $C_1$-$C_2$ | 1.45 | $C_1$-$C_2$-$H_4$ | 116.2 |
| $C_2$-N | 1.28 | $H_4$-$C_2$-N | 122.2 |
| N-$C_3$ | 1.42 | N-$C_2$-$C_1$ | 121.6 |
| All C-H | 1.08 | $C_2$-N-$C_3$ | $\phi^a$ |
| All ring C-C | 1.39 | θ, γ, and $\beta^b$ | 0 |

[a] Variable (see text). [b] This defines β as the dihedral angle between the $C_1$-$C_2$ and N-$C_3$ bonds *minus* 180°.

## Results

**Ground-State Conformations.** The energy of NBA was first calculated as a function of the angles φ and θ with ring B and the nuclei $C_2$, N, and $H_4$ fixed in a plane ($\gamma = \beta = 0°$). The resulting energy surface is shown in Figure 2. Two well-defined minima at $\theta = 90°$, $\phi = 117°$, and $\theta = 90°$, $\phi = 225°$ are found which are separated by an energy barrier at $\theta = 90°$, $\phi = 180°$. The two minima clearly correspond to trans and cis configurations, respectively, of the molecule. It is noteworthy that both isomers, as defined by this energy contour, have conformations in which ring A is perpendicular to the plane of the rest of the molecule.

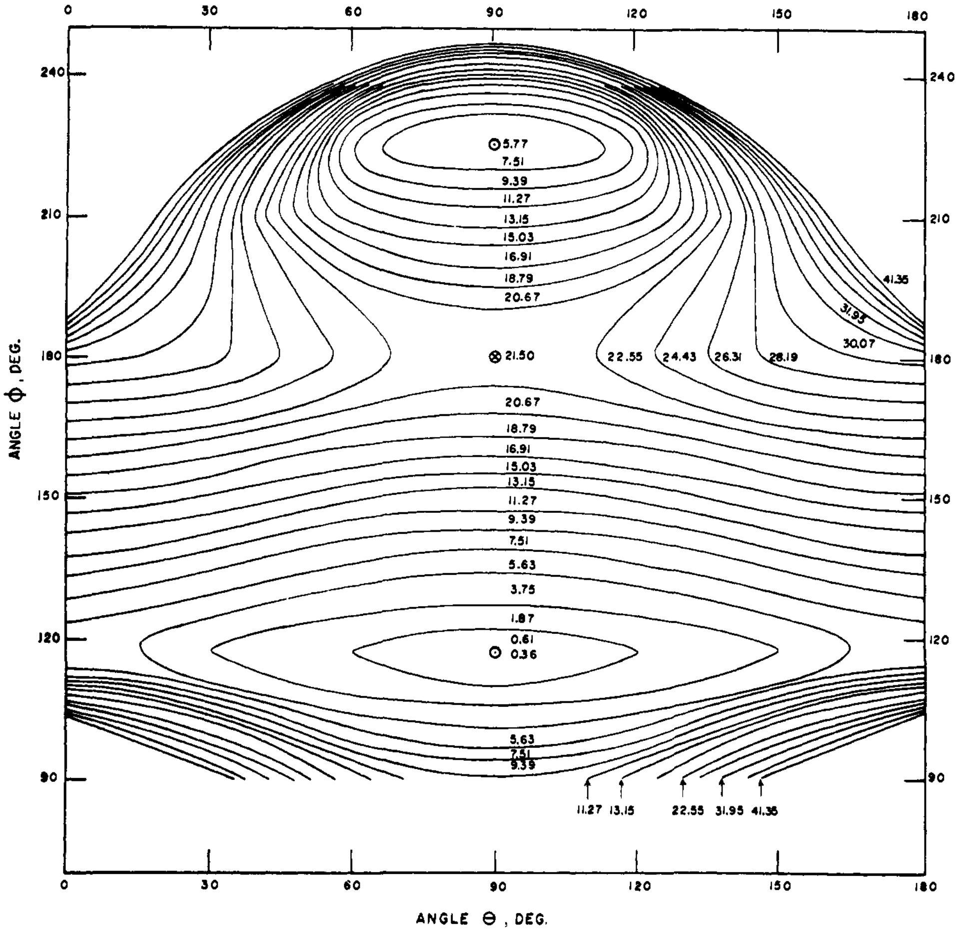

Figure 2. Energy of NBA as a function of angles φ and θ with angles $\gamma = \beta = 0°$. The labels represent the energy in kilocalories per mole relative to a value of zero for the minimum-energy trans conformation (see text).

In order to check the validity of the assumption that ring B and the C=N moiety are coplanar, the energy was calculated as a function of the angle γ for the cases $\theta = 90°$, $\phi = 180°$ (trans configuration), $\theta = 90°$, $\phi = 225°$ (cis configuration), and $\theta = 90°$, $\phi = 180°$ (saddle point X, Figure 2). The results (Figure 3) show shallow minima at $\gamma = 53°$ for the trans case, at $\gamma = 30°$ for the cis case, and at $\gamma = 30°$ for the linear configuration, corresponding to energy decreases of 0.36, 0.32, and 0.06 kcal/mol, respectively, relative to $\gamma = 0°$. Since *kT* corresponds to *ca.* 0.6 kcal/mol at room temperature,

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(14) J. Bergman, L. Leiserowitz, and G. M. J. Schmidt, *J. Chem. Soc.*, 2068 (1964); J. Bergman, L. Leiserowitz, and K. Osaki, *ibid.*, 2086 (1964).

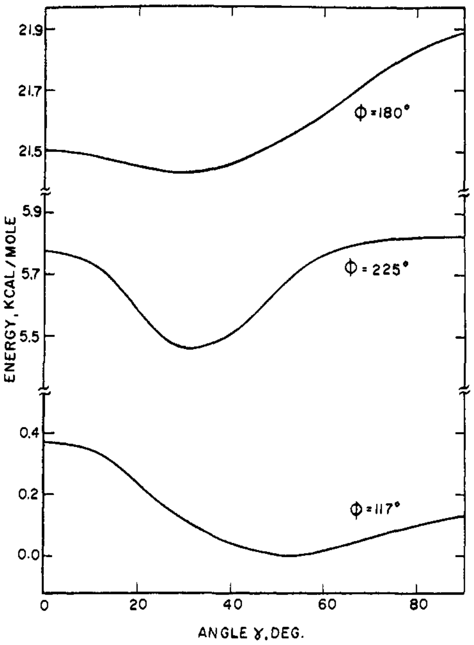

Figure 3. Energy of NBA as a function of the angle of twist ($\gamma$) of ring B for the minima and saddle point X of Figure 2. Angle $\theta$ = 90° in all cases.

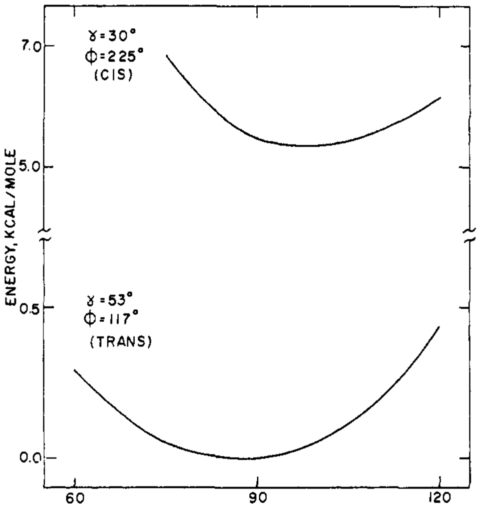

Figure 4. Energy of NBA as a function of angle $\theta$ for the cis ($\phi$ = 225°, $\gamma$ = 30°) and trans ($\phi$ = 117°, $\gamma$ = 53°) conformations.

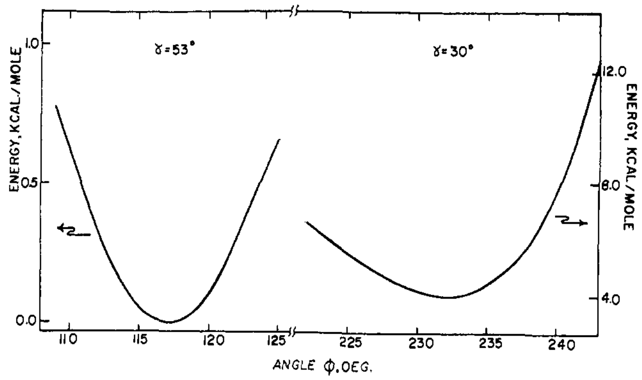

Figure 5. Energy of NBA as a function of angle $\phi$ for the cis ($\gamma$ = 30°) and trans ($\gamma$ = 53°) conformations with $\theta$ = 90°.

we expect that for the conformations corresponding to the extrema of Figure 2, ring B will have essentially free rotation under ordinary conditions.

The variation of the energy for $\gamma = 30°$ and 53° (corresponding to the cis and trans forms, respectively) with the angles $\theta$ and $\phi$ in the vicinity of the values associated with the energy minima for $\gamma = 0°$ is shown in Figures 4 and 5. For $\gamma = 53°$, the energy minimum remains unshifted at $\phi = 117°$ and $\theta = 90°$, and, in view of the small variation of the energy with $\gamma$, the corresponding point in Figure 2 adequately represents the trans configuration with respect to these three degrees of freedom. On the other hand, the minimum-energy cis configuration is not well approximated by Figure 2. Thus we find the minimum for $\phi = 225°$, $\gamma = 30°$ to be shifted from $\theta = 90°$ to $\theta = 100°$ (decrease of *ca.* 0.1 kcal/mol), and that for $\theta = 90°$, $\gamma = 30°$ to appear at $\phi = 233°$ instead of at $\phi = 225°$ (decrease of *ca.* 1.5 kcal/mol). The factor primarily responsible for these angle changes is readily identified by inspection of a molecular model as steric interference between rings A and B. When the two rings are perpendicular to each other, compression tends to force them apart, thereby causing a decrease in angle $\phi$. In reality, the distortion is undoubtedly partitioned between $\phi$ and the N=C—$C_6H_5$ (B) angle, but this does not show up in our calculations since the latter angle was arbitrarily held constant.

Since it is evident that another degree of freedom (angle $\gamma$) becomes important as the cis structure is approached, the $\phi$–$\gamma$ energy surface was constructed for $\theta = 90°$ and $\phi > 220°$ to locate the minimum energy of the cis configuration. As shown in Figure 6, the minimum appears at $\phi = 253°$, $\gamma = 53°$. Variation of $\theta$ with $\phi$ and $\gamma$ fixed at these values established that $\theta$ = 90° corresponds to the minimum energy. This true minimum is 5.55 kcal/mol lower than the cis structure minimum in Figure 2. At this point we may summarize the results as follows. The three-dimensional $\phi$–$\theta$–$\gamma$ energy surface has two minima, one corresponding to *trans*-NBA at −112.2560 au with $\phi = 117°$, $\theta = 90°$, and $\gamma = 53°$, and the other corresponding to *cis*-NBA at −112.2556 au with $\phi = 253°$, $\theta = 90°$, and $\gamma = 90°$. This places the cis structure 0.23 kcal/mol above the trans structure.

It has already been pointed out that, for the trans compound, ring B can rotate freely at room temperature. The barrier to rotation for ring A is calculated to be *ca.* 7 kcal/mol. However, the potential well for angle $\theta$ is quite shallow near the bottom (*cf.* Figure 4), and a 30° twist of $\theta$ about 90° changes the energy by less than 0.5 kcal/mol, so that thermal oscillation of ring A can be expected at room temperature. For the cis configuration, free rotation is clearly impossible for both rings. The cross sections of the potential wells for $\phi = 253°$ are shown in Figure 7. They indicate that the energy is a more rapidly varying function of $\theta$ than of $\gamma$ for angles outside 90 ± 20°. Both wells are reasonably shallow near the bottom, and the variation of $\theta$ or $\gamma$ by ±25° is accompanied by an energy increase of less than 0.6 kcal/mol.

The dipole moments calculated for the minimum-energy *trans*- and *cis*-NBA conformations and for a planar trans conformation are compared with experimental values in Table II.

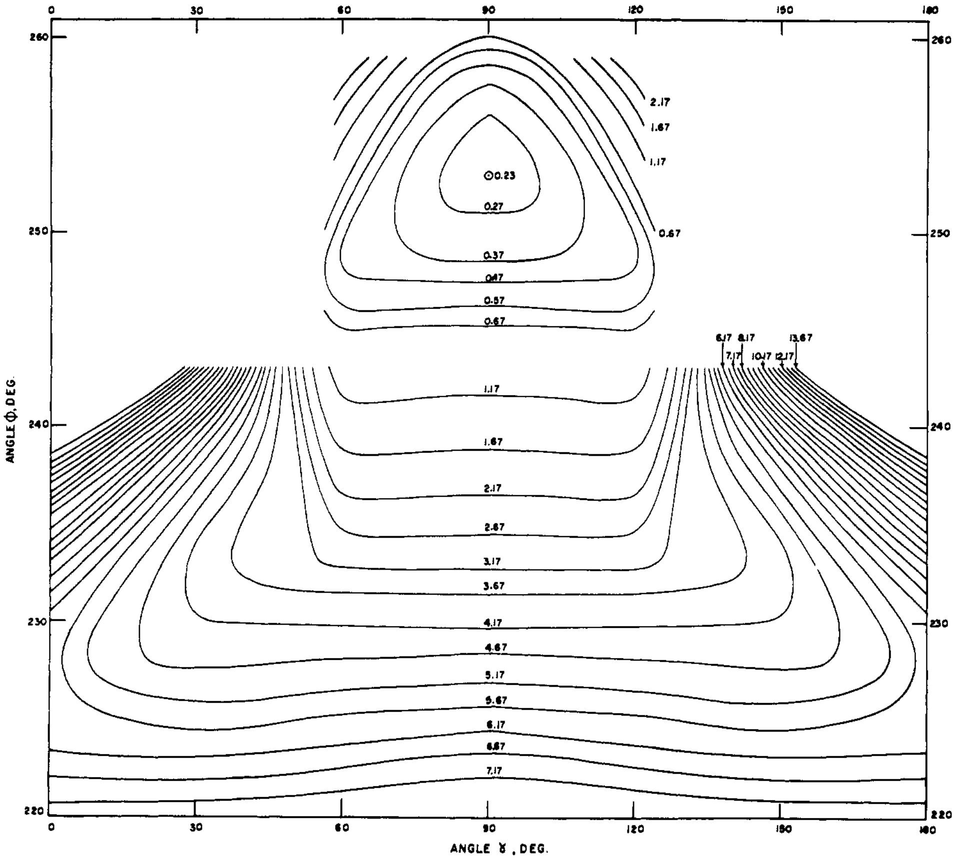

Figure 6. Energy of NBA as a function of angles $\phi > 220°$ and $\gamma$ with angles $\theta = 90°$, $\beta = 0°$. The energies are indicated in kilocalories per mole relative to the minimum-energy trans conformation.

**Isomerization.** Interconversion between cis and trans forms of NBA can be envisioned to occur by inversion about the nitrogen atom (increase in angle $\theta$) or by rotation about the C–N double bond (angle $\beta$, Figure 1). The energy surfaces of Figures 2 and 6 provide the pertinent information for the former path. Since the minimum-energy conformations of *cis*- and *trans*-NBA both have $\theta = 90°$, this degree of freedom is apparently not important in the interconversion of the two forms by inversion. The reaction coordinate is complex, and its specification requires consideration of the simultaneous motion of the angles $\phi$ and $\gamma$. The numerical results, however, clearly indicate that the barrier to isomerization by inversion is predominantly determined by variation of the angle $\phi$. For this path the intermediate state is considered to be the linear conformation $\phi = 180°$, $\theta = 90°$, $\gamma = 30°$, and $\beta = 0°$ (energy $-112.2218$ au) which, in view of the minor influence of $\gamma$ on the energy (*cf.* Figure 3), is well approximated by the saddle point X of Figure 2 ($\phi = 180°$, $\theta = 90°$, $\gamma = \beta = 0°$). For isomerization by rotation, the conformation in which the dihedral angle between the $C_1$–$C_2$ and N–$C_3$ bonds is 90°, *i.e.*, $\beta = -90°$, $\theta = 90°$, $\gamma = 0°$, $\phi = 117°$, is considered to approximate the intermediate state. The energies of the two intermediate conformations are compared in Table III.

**Table II.** Calculated and Observed Dipole Moments of NBA

| Isomer | Conformation,[a] deg $\phi$ | $\theta$ | $\gamma$ | Dipole moment, D Calcd | Obsd |
|---|---|---|---|---|---|
| Trans | 117 | 90 | 53 | 1.83 | 1.57[b]<br>1.60[c] |
| Trans (planar) | 117 | 0 | 0 | 1.75 | |
| Cis | 253 | 90 | 90 | 2.10 | |

[a] With $\beta = 0°$. [b] V. de Gaouck and R. J. W. Le Fevre, *J. Chem. Soc.*, 741 (1938). [c] V. I. Minkin, O. A. Osipov, and V. A. Kogan, *Dokl. Akad. Nauk SSSR*, **145**, 236 (1962).

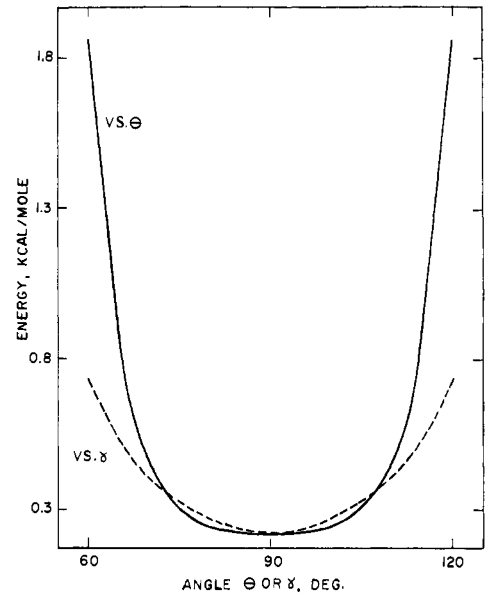

Figure 7. Energy of NBA as a function of angles $\theta$ and $\gamma$ for the minimum of Figure 6 ($\phi = 253°$).

Table III. Energies of Intermediate Conformations for Isomerization

| Path | Intermediate conformation, deg $\alpha$ | $\theta$ | $\gamma$ | $\beta$ | Energy, kcal/mol[a] |
|---|---|---|---|---|---|
| Inversion | 180 | 90 | 30 | 0 | 21.44 |
| Rotation | 117 | 90 | 0 | −90 | 60.40 |

[a] Relative to zero for the trans configuration ($\phi = 117°$, $\theta = 90°$, $\gamma = 53°$, $\beta = 0°$).

It might be argued that rotation about the C–N bond is accompanied by additional motions, namely elongation of this bond and of the bonds linking these atoms to the benzene rings. No calculations were performed with NBA to assay the importance of these motions, but the results of CNDO calculations on the analogous intermediate for the isomerization of stilbene indicate that bond stretching at the top of the rotation barrier is negligible.[15] Calculations on the inversion intermediate for azobenzene, which has a similar structure to that of NBA, also show the pertinent bonds to remain constant in length.[15] The results given in Table III thus leave little doubt that rotation about the C–N double bond is associated with a substantially higher energy barrier than inversion at the nitrogen atom.

If the zero-point energies of the intermediate and stable conformations are assumed to cancel, the barrier to cis → trans isomerization by inversion is estimated to be 21.2 kcal/mol. For the trans → cis process, the barrier is *ca.* 0.25 kcal/mol higher. On the trans side, the reaction coordinate for isomerization may, to a good approximation, be represented by the angle $\phi < 180°$ at $\theta = 90°$, $\gamma = \beta = 0°$. The change of angle $\gamma$ evidently occurs predominantly on the cis side of the barrier ($\phi > 180°$) so that descent to the cis structure involves the correlated increase of angles $\phi$ and $\gamma$. The general shape of this path is apparent in Figure 6.

## Discussion

In general, the results of the calculations agree quite well with what is known about NBA. Two isomers of NBA have been characterized, and the calculations predict two well-defined isomers—a trans configuration with the valence angle $\phi = 117°$ and a cis configuration with $\phi = 253°$. Experimentally, the trans isomer is found to be the more stable of the two species. In at least qualitative agreement with this finding, the energy of the cis isomer is calculated to be 0.23 kcal/mol larger than that of the trans isomer.

Experimentally, the equilibrium between the two isomers of NBA appears to favor the trans form more than the small calculated energy difference indicates. The enthalpy change for the trans–cis interconversion has not been measured, but the nmr spectrum of NBA in deuteriochloroform at room temperature, which shows a single line at $\tau$ 1.58 ppm due to $H_4$ (*cf.* Figure 1), indicates that the solution contains exclusively one isomer. Moreover, a larger energy difference is also to be anticipated on the basis of comparison with the properties of stilbene and azobenzene. For these compounds, the enthalpy changes associated with the cis → trans conversion are 2.3–2.9 kcal/mol (solution)[16] and 9.9 kcal/mol (solid),[17] respectively. In attempting to correlate the calculated energy difference with experimental thermodynamic data we are, of course, neglecting the effect of temperature and of steric factors which may well be substantial inasmuch as both the calculations and molecular models indicate that internal motions are more hindered in the cis configuration than in the trans configuration. We are, however, inclined to believe that the apparent error in the magnitude of the energy difference has a more basic cause and that it reflects the particular parametrization employed as well as the effect of neglecting potentially significant degrees of freedom, in particular the N=C—$C_6H_5$ (B) valence angle.

The prediction of the CNDO calculations that the minimum-energy trans conformation of NBA is nonplanar agrees with the results obtained by Hückel molecular orbital theory.[6–8] Houlden and Csizmadia's study,[9] which utilized extended Hückel theory, is not pertinent to the question of the orientation of the benzene rings since these authors assumed NBA to be planar. The minimum-energy conformation of *trans*-NBA calculated by us ($\phi = 117°$, $\theta = 90°$, $\gamma = 53°$) may be compared with the structure determined in the crystalline state by X-ray measurements ($\phi = 119.9°$, $\theta = 55°$, $\gamma = 170°$). This experimental structure may be viewed as having rings A and B twisted out of planarity in opposite directions. Both the calculated and experimental conformations have an angle $\phi$ which is close to that for $sp^2$ hybridization at the nitrogen atom. The calculated results pertain, of course to the isolated molecule. It is to be expected that incorporation of the molecule in the crystal will be accompanied by some distortion, particularly if certain motions have small energy requirements. The calculations indicate that, for NBA, rotation of the rings is most likely to be involved in such structural adaptation to the environment. On a quantitative basis, it has been calculated that the conversion of the minimum-energy form to the experimental structure requires an energy of about 1 kcal/mol. An energy difference of this magnitude can certainly be accounted for by stabilization accruing from the preferred packing arrangement in the crystal. A more meaningful evaluation of the correctness of the calculated conformation would, of course, be based on the comparison with the structure determined in the gas phase. Unfortunately, this information is not available at this time. It has been pointed out that, since the crystal reflectance spectrum of NBA is similar to the solution spectrum, the stable conformation of the free molecule is not too different from that in the crystal.[3] Our results tend to bear out this proposal.

The CNDO calculations on NBA provide significant information about the barriers to rotation of the benzene rings and about the importance of conjugative interaction of the nitrogen-centered lone-pair electrons and of the C–N $\pi$ system with the rings. Hückel molecular orbital theory, by concerning itself solely with $\pi$ electrons, tends to overemphasize conjugation effects. Moreover, meaningful conformational calculations based on this method must be augmented by the separate consideration of steric factors. The CNDO method has the advantage that both effects are treated within the same theoretical framework.

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(15) S. Ljunggren and G. Wettermark, unpublished results.

(16) G. Fischer, K. A. Muszkat, and E. Fischer, *J. Chem. Soc. B*, 1156 (1968).

(17) R. J. Corricini and E. C. Gilbert, *J. Amer. Chem. Soc.*, **61**, 2925 (1939).

According to the calculations, there is essentially free rotation of ring B in *trans*-NBA. Although the magnitude of the rotation barrier is determined by the interplay of conjugative and steric factors we nonetheless infer from this result that $\pi$ conjugation between the C–N double bond and ring B is not extensive and that, consequently, the $C_1$–$C_2$ bond has little double-bond character.[18] The same conclusion follows from the experimentally determined length of 1.496 Å for this bond,[3] which is close to the normal C–C single-bond distance of 1.54 Å.

The rotation barrier for ring A ($\sim$7 kcal/mol) is substantially larger than that for ring B (0.36 kcal/mol). In this case the barrier may be considered to represent the balance between steric hindrance and conjugative interactions involving ring A and respectively the C–N double bond and the nitrogen lone-pair electrons. The relative contributions from these sources are difficult to assess, but it seems unlikely that stabilization due to the nitrogen lone pair–$\pi$ interaction with the ring amounts to more than a few kilocalories. In concluding this discussion of the structure of *trans*-NBA, we may note that the results of CNDO calculations on the trans isomers of stilbene and azobenzene are entirely consistent with the present study.[15] For both molecules it was found that the nonplanar conformation in which the benzene rings are perpendicular to the C—C=C—C (or C—N=N—C) plane is a few kilocalories per mole less energetic than the corresponding planar conformation. Thus $\pi$ interaction with the double bond is evidently outweighed by steric factors in one case and by nitrogen–ring n–$\pi$ conjugation in the other.

There are no experimental data on the structure of the unstable *cis*-NBA. The perpendicular (to the C—C=N—C plane) disposition of both rings in the minimum-energy conformation of this configuration is clearly the result of steric hindrance.

The calculated dipole moment of *trans*-NBA (Table II) is in reasonable agreement with the experimental values. As is to be expected from its structure, the moment calculated for the cis isomer is larger than that for the trans isomer. The calculation of the dipole moment of NBA by the group and link-moment addition method has been reported.[19] For a planar trans configuration, satisfactory agreement with the measured value could be obtained by inclusion of a variable mesomeric moment.[20]

The calculations indicate that NBA isomerizes by inversion at the nitrogen atom rather than by rotation about the C–N double bond. The calculated barrier for cis → trans conversion by inversion is 21.2 kcal/mol, which may be compared with the experimental activation energy of 16.5 kcal/mol.[5] Implicit in this conclusion is the assumption that the barrier to rotation is not substantially lowered by a crossover from the singlet ground-state energy surface to an excited-state surface. For the thermal isomerization of stilbene there is experimental and theoretical evidence that a transition of this nature is unimportant.[21] The inversion path for the interconversion of anil isomers gains support from the observations of Jeffery, Meisters, and Mole,[22] who studied the effect of complex formation on the isomerization of *N*-($\alpha$-methyl)benzylideneaniline. These authors reasoned that involvement of the nitrogen lone-pair electrons in bonding with a Lewis acid should block isomerization by inversion while still permitting it to occur by rotation. Since the complexed anil was found not to isomerize, it was inferred that the inversion mechanism predominates.

Somewhat different conclusions were reached by Gordon and Fischer,[23] who used the INDO method[24] in a theoretical study of the isomerization of diazacumulenes ($R—N{=}(C)_n{=}N—R$). For these compounds the mechanism appears to depend on the chain length. Thus diimide ($R = H$, $n = 0$) is predicted to isomerize by inversion while for carbodiimide ($R = H$, $n = 1$) the energy requirements for rotation and inversion are about equal. It is also of interest to note that application of the method of localization energies[25] to the isomerization of anils provides results which are consistent with a rotation mechanism.[26] Thus the logarithm of the rate constant of cis–trans isomerization for a number of anils is found to be linearly related to the bond order and the "localization energy for cis–trans isomerization" (LEI) of the isomerizing bond ($C_2$–N for NBA). The rotation mechanism enters the picture through the LEI, which is defined as the calculated difference between the $\pi$ energy of the unperturbed molecule and the $\pi$ energies of the two radical fragments obtained by reducing the $\pi$ interaction of the isomerizing bond to zero. The mechanistic implications of LEI calculations must, however, be treated with caution since the method is based entirely upon simple $\pi$-electron molecular orbital theory.

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(18) Actually, the calculations tend to exaggerate both conjugative and steric interactions since they are based on a $C_1$–$C_2$ distance which is smaller by 0.5 Å than the experimental distance (*cf.* Table I).

(19) E. Hertel and M. Schinzel, *Z. Phys. Chem., Abt. B*, **48**, 289 (1941).

(20) F. Feichtmayr and F. Würstlin in "Festschrift Carl Wurster zum 60. Geburtstag," Ludwigshafen/Rhein, Germany, 1960, p 177.

(21) *Cf.* P. Borrell and H. H. Greenwood, *Proc. Roy. Soc., Ser. A*, **298**, 453 (1967).

(22) E. A. Jeffery, A. Meisters, and T. Mole, *Tetrahedron*, **25**, 741 (1969).

(23) M. S. Gordon and H. Fischer, *J. Amer. Chem. Soc.*, **90**, 2471 (1968).

(24) J. A. Pople, D. L. Beveridge, and P. A. Dobosch, *J. Chem. Phys.*, 47, 2026 (1967).

(25) G. W. Wheland, *J. Amer. Chem. Soc.*, **64**, 900 (1942).

(26) G. Wettermark in "Fast Reactions and Primary Processes in Chemical Kinetics," Nobel Symposium, No. 5, S. Claesson, Ed., Almqvist and Wiksell, Stockholm, 1967, pp 391–399.