

An *ab initio* study of the conformational energetics of Nbenzylideneaniline

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An *ab initio* study of the conformational energetics of *N*-benzylideneaniline

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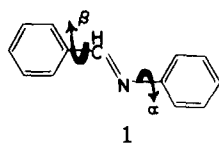
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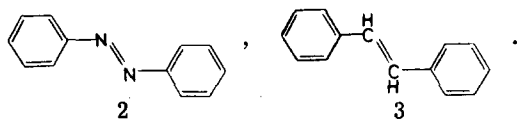
Ab initio calculations employing both minimal (STO-4G) and split valence (4-31G) basis sets have been used to study the conformational energy surface of *N*-benzylideneaniline (NBA). The former indicate that the minimum energy conformation of NBA corresponds to a rotation about the N-phenyl bond of $\approx 45^\circ$ and a rotation about the CH-phenyl bond of 0° . These results are in close correspondence with those from spectroscopic and x-ray diffraction studies. This represents a significant improvement over the results obtained from most semiempirical methods which in general have not been able to account for the rotation about the exocyclic bonds. The compounds *N*-ethylideneaniline and *N*-methylbenzylidenimine were also studied and found to be good models for determining the energetics about the two exocyclic single bonds using both the minimal and extended (4-31G) basis sets. A partitioning of the results for these two model compounds yields information which permits an analysis of the origin of the barrier to a planar conformation in benzylideneaniline as well as the difference between the two basis sets. The partitioning also provides a criterion for determining the suitability of particular compounds as models for larger systems. The most stable conformation of NBA has been attributed to a compromise between steric interactions and delocalization of the bridge double bond and/or nitrogen lone pair electrons into the conjugated system. Calculations on additional model compounds were carried out in an attempt to isolate the relative contributions of these factors in determining the most stable conformation. Finally, electron deformation plots have been employed in order to gain insight into the features of the electron density distribution underlying these effects.

INTRODUCTION

In the course of a recent study of the influence of crystal forces on molecular conformation¹—conformational polymorphism—we required fairly detailed information on the conformational energetics of *N*-benzylideneaniline (NBA):



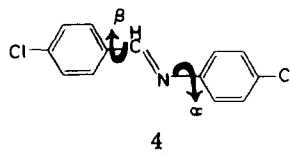
This compound has received a great deal of attention since it was recognized² that the electronic optical spectrum differs markedly from its isoelectronic analogs *trans*-azobenzene and *trans*-stilbene:



A number of x-ray crystal structure determinations have shown that compounds 2^{3(a)} and 3^{4(a)} are essentially planar in the solid state, while gas-electron diffraction studies^{3(b),4(b)} indicate that the phenyl groups may be rotated by up to 30° about the exocyclic single bonds. However, the correspondence between spectral properties in solution and the solid for both of these compounds⁵ suggests that the molecules are planar, or nearly so, in solution. NBA, on the other hand, is non-

planar in the solid,^{6(a)} in the gas phase,^{6(b)} and in solution.^{6(c)} In geometric terms, the nonplanarity manifests itself in nonzero values for the two parameters which define the molecular conformation: the torsion angle (α) about the N-phenyl bond which has been determined to be 55.0° in the solid^{6(a)} and 52° in the gas phase (by electron diffraction)^{6(b)}; that about the CH-phenyl (β) which is -10.3° in the solid^{6(a)} and was assumed to be zero in the gas phase.^{6(b)}

Spectroscopic investigations⁷ very strongly suggested that the difference in spectral properties could be directly attributed to the conformational change, and this hypothesis was given added weight when the diffuse reflectance spectrum of NBA in the solid,⁸ where the molecule is known to be nonplanar,^{6(a)} was shown to resemble that observed in solution. The discovery of a planar conformation in the triclinic crystalline polymorph of dichlorobenzylideneaniline⁹ DCBA



led to the direct proof of the hypothesis previously based on inferences from spectroscopic evidence. In the solid the spectrum of this form of DCBA¹⁰ resembles that of compounds 2 and 3, while the solution spectrum is similar to that of NBA. DCBA also crystallizes in an orthorhombic form,¹¹ wherein the molecular conformation ($\alpha = -\beta = 24.8^\circ$) is significantly nonplanar. This system of

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conformational polymorphs formed the basis for our earlier theoretical and spectroscopic studies.^{1,10}

Some of the most recent work on NBA has been concerned with the energetics of the molecular conformation in order to understand the reasons for the tendency to nonplanarity. Haselbach *et al.*⁷ measured and analyzed the PE spectrum of NBA and reported approximate values of $\alpha \sim 36^\circ$ and $\beta \sim 0^\circ$ for the gas phase conformation. By comparison with analogous compounds, including compounds **2** and **3**, they reached the conclusion that semiempirical methods (MINDO/2, CNDO/2, and MINDO/3) are not applicable to systems of this type and suggested that in general these methods are not reliable for treating torsional energies about essential single bonds which connect π systems. However, two recent semiempirical studies,¹² employing geometry optimization with PCILO and CNDO/2, did produce a minimal energy conformation close to that observed in the solid^{6(a)} and determined in the gas phase.⁷

The principal purpose of the study undertaken here was to obtain a better understanding of the factors responsible for the conformational behavior of these compounds and improved *ab initio* estimates of the torsional energetics about α and β . In addition, we would like to test directly the validity of the use of additivity when *ab initio* calculations are carried out on small model compounds for the investigation of conformational parameters in large systems. Thirdly, we wished to examine the basis set dependence of the results for the compound studied. Finally, we wanted to isolate the relative contributions of steric interactions and electron delocalization in determining the most stable conformation of NBA.

METHOD

Calculations were performed with both the GAUSS 70 program^{13(a)} and the GAUSS 100 program^{13(b)} employing both the minimal basis set (STO-4G) and, where possible, the extended basis set (4-31G) (see below). The use of two different basis sets was suggested by a recent study¹⁵ in which it was shown that minimal and extended basis sets can lead to significantly different predictions for the energetics of rotations about the N-C α and C α -C' bonds of methyl groups in amide and peptide systems. It was later shown¹⁶ that the electron density for these systems as described by the minimal basis set constrains the electrons to a region too close to the nucleus, resulting in atoms whose "radii" are too small. This in turn can affect the calculated conformational equilibria.

For calculations on NBA, bond lengths and bond angles were taken from Ref. 6(a).

To test the additivity of energies obtained from calculations on model compounds¹ and the dependence of these results on basis set we studied in detail the energetics of the model compounds *N*-ethylideneaniline (NEA) (**5**) and *N*-methylbenzylideneimine (NMBI) (**6**) (for α and β , respectively) employing both minimal and extended basis sets:

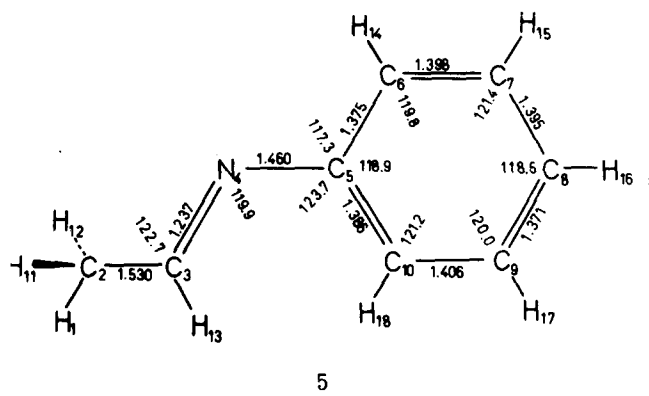


TABLE I. STO-4G energies for NBA, including partitioning.^a

	Conformation			
	$\alpha = 24.8^\circ, \beta = 0^\circ$	$\alpha = -\beta = 24.8^\circ$	$\alpha = 45^\circ, \beta = 0^\circ$	$\alpha = 0^\circ, \beta = 45^\circ$
Kinetic energy	-8.20	-9.31	-0.79	-18.43
Nuclear-electronic	245.26	356.90	552.08	639.26
Electron repulsion	-123.76	-184.05	-283.74	-323.67
Nuclear repulsion	-114.49	-163.73	-298.73	-264.73
Total	-1.18	-0.19	-1.57	2.82

^aEnergies given here in kcal are the differences between those for the conformation listed and the planar molecule $\alpha = \beta = 0^\circ$.

The conformation found in the orthorhombic structure of DCBA ($\alpha = -\beta = 24.8^\circ$), in which disorder is present, is calculated to be about 0.2 kcal more stable than the planar one with the STO-4G basis set. The energy difference between this conformation and the one where only α differs from 0° suggests that rotation about the C-phenyl bond (i.e., β) is a destabilizing conformational perturbation, with a rotation of 24.8° destabilizing by a ~ 1 kcal. This is consistent with the observation that in all nondisordered crystal structures of benzylideneaniline, β maintains a value close to 0° .^{6(a)} For the conformation $\alpha = 0^\circ, \beta = 45^\circ$, the energy is significantly higher (by 2.82 kcal) than for the planar molecule. Hence, there is quite convincing evidence that to 45° , at least, rotations about the N-phenyl bond (α) are stabilizing, while those about the C-H phenyl bond (β) are destabilizing.

Energetics about α and β : The model compounds

The calculations for the model compounds NEA and NMBI are intended to give quantitative estimates of the total energetics about, respectively, α and β in the parent molecule; the results are summarized in Figs. 1 and 2 and Table II. The electron deformation density maps show that for NEA [Fig. 2(a)] the *ortho* hydrogen is in closer proximity to the hydrogen atom of the bridge than the same hydrogen on NMBI [Fig. 2(b)] is to the lone pair on the bridge nitrogen, consistent with a greater repulsion in the former. The short $H \cdots H$ distance of 1.8 Å along with these considerations suggests the possibility of a nonbonded $H \cdots H$ repulsion in NEA, which, if present in NMBI, is only so to a much lesser extent. Also worthy of note is the fact that the maximum electron density for the two bonds adjacent to the nitrogen lone pairs in both compounds lies off the internuclear axis and in all cases away from the nitrogen lone pair. Hence, there is a suggestion of "bent bonds" in these cases which may be attributed to repulsion of these bonding densities by the lone pair electrons on the nitrogen atom.

Table II includes partitioning of the energy into kinetic, nuclear-electron attraction, and electron and nuclear repulsion contributions¹⁶ to permit analysis of the conformational energetics about the N-phenyl and CH-phenyl bonds and to reveal details of the sources of any

differences between basis sets.

In terms of general trends of overall energies the two basis sets yield similar results (Fig. 2). As in the full molecule, rotations from the planar conformation in α are stabilizing to 45° , while those for β are destabilizing. In all cases the STO-4G basis set yields a lower estimate for the stabilization (for α) or destabilization (for β) as a result of increasing torsion angle as compared to the 4-31G basis set by about 10%–15%. The minimum energy for α (at 45°) is -1.99 kcal (STO-4G) and -2.21 kcal (4-31G).

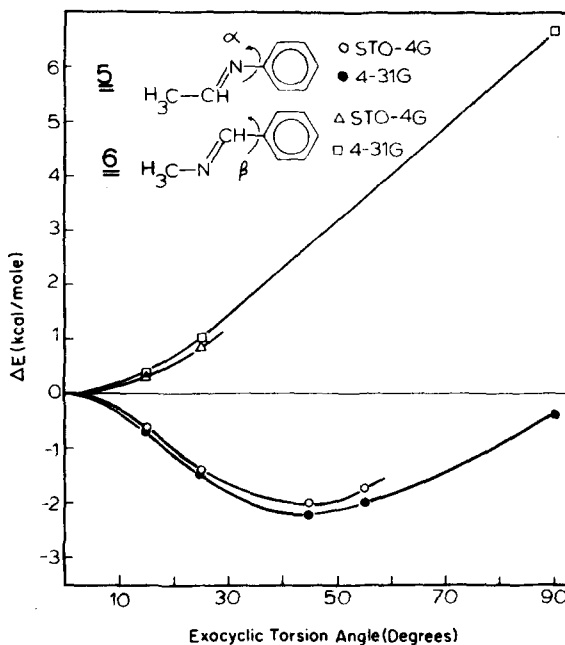


FIG. 1. Summary of *ab initio* calculations on compounds 5 and 6. The points labeled STO-4G were obtained using a minimum basis set while those labeled 4-31G were obtained using an extended basis set in GAUSS 70¹⁵ and GAUSS 100.¹⁶ The ordinate represents energy differences between the planar conformation (0°) and nonplanar ones. The points at 25° represent the nonplanar conformation found in the orthorhombic structure of compound 4, which clearly is not the minimum energy conformation. On the basis of these calculations the minimum energy conformation for benzylideneaniline NBA would correspond to $\alpha = 45^\circ, \beta = 0^\circ$.

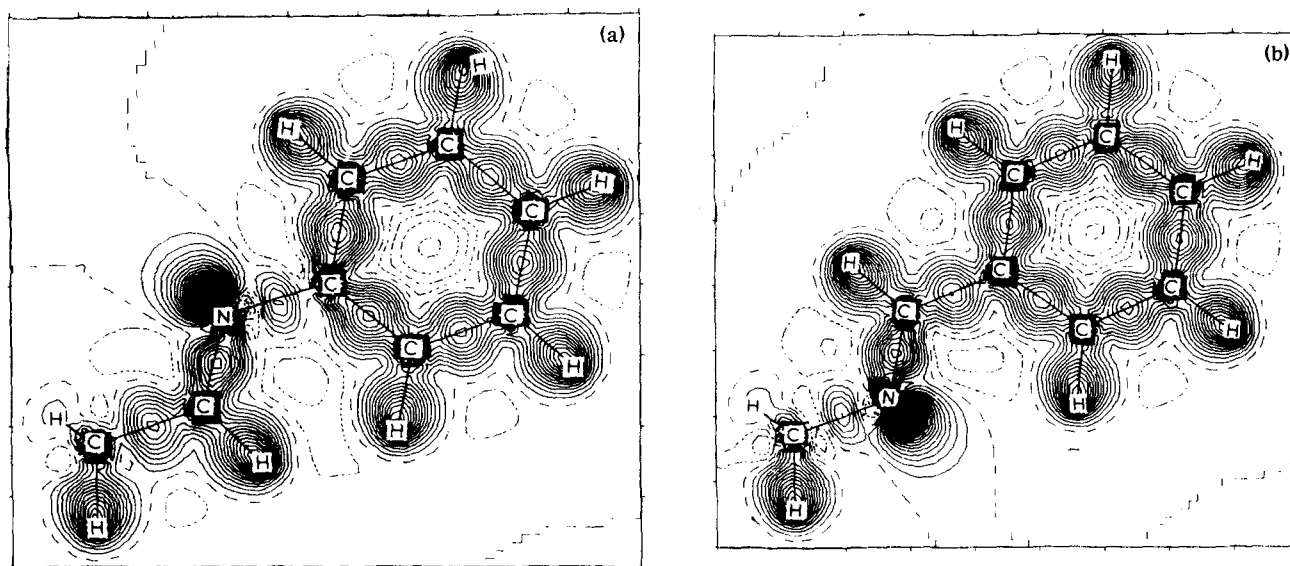


FIG. 2. Deformation electron density maps for *N*-ethylideneaniline (a) and *N*-methylbenzylideneimine (b) in the planar conformation ($\alpha = 0^\circ$, $\beta = 0^\circ$) as calculated with the extended 4-31G basis set. Countour intervals are $0.05/\text{\AA}^3$; solid lines indicate positive electron density, broad broken lines the zero level of electron density, and firm broken lines regions of negative electron density. The methyl hydrogens are shown in projection on the plane of the molecule.

The equilibrium conformation for NBA obtained directly from minimal basis set calculations and by extrapolation from the model compounds treated here (i. e., $\alpha = 45^\circ$, $\beta = 0^\circ$) thus agrees well with the free molecule conformation generally accepted by spectroscopists on the basis of recent spectral measurements⁷ and with the conformation found in a number of crystal structures.^{6(a),19} These results also strongly suggest that *ab initio* methods, regardless of basis set, are definitely preferable to the semiempirical methods (MINDO/2, CNDO/2, MINDO/3, and PCILO) for treating two pi systems connected by an essential single bond. The latter methods yield variable results. In studies where geometry optimization is employed,¹² they predict the correct conformation, albeit yielding bond angles

and bond lengths which differ significantly from those found in crystal structures. Without inclusion of geometry optimization^{7,20} the same methods predict a value of 90° for α and/or β .

A natural question at this point, then, is "what does an *ab initio* calculation predict for the extremes in conformation given by the semiempirical methods as the minimum?" To obtain more detailed information on this point we carried out the calculation for torsion angles of 90° on both NEA and NMBI employing the extended basis set (Table II and Fig. 1). The energy obtained for $\alpha = 90^\circ$ is lower than for $\alpha = 0^\circ$ by 0.4 kcal but is significantly above the minimum at $\alpha = 45^\circ$. The corresponding energy for $\beta = 90^\circ$ is 6.7 kcal above the planar one, and

TABLE II. Partitioning of the barrier to rotation about the (a) N-phenyl bond (model compounds) and (b) CH-phenyl bond (model compound 6) in STO-4G and 4-31G.^a

<i>N</i> -ethylideneaniline (NEA)										
	$\Delta E_{15.0}$		$\Delta E_{24.8}$		$\Delta E_{45.0}$		$\Delta E_{55.0}$		$\Delta E_{90.0}$	$\Delta[\Delta E_{45.0}]$
	STO-4G	4-31G	STO-4G	4-31G	STO-4G	4-31G	STO-4G	4-31G	4-31G	$[(4-31G) - (STO-4G)]$
Kinetic energy	-3.65	-3.56	-8.84	-8.32	-19.96	-17.43	-24.15	-20.30	-24.0	2.53
Nuclear-electron	76.29	74.17	194.23	187.99	503.12	483.35	639.61	612.68	687.65	-19.77
Electron repulsion	-37.86	-35.89	-96.61	-91.01	-251.38	-234.38	-320.24	-297.38	-334.21	17.01
Nuclear repulsion	-35.41	-34.41	-90.15	-90.15	-233.75	-233.75	-296.94	-296.94	-329.82	0
Total	-0.64	-0.69	-1.37	-1.49	-1.99	-2.21	-1.73	-1.94	-0.38	-0.22
<i>N</i> -methylbenzylideneimine (NMBI)										
Energy Component	$\Delta E_{15.0}$		$\Delta E_{24.8}$		$\Delta E_{90.0}$		$\Delta(\Delta E_{24.8})[4-31G](STO-4G)$			
	STO-4G	4-31G	STO-4G	4-31G	4-31G					
Kinetic energy	-0.36	0.01	-0.81	0.28	7.68	1.09				
Nuclear-electron	55.88	54.87	145.05	142.13	685.41	-2.92				
Electron repulsion	-29.19	-28.50	-75.72	-73.74	-353.79	1.98				
Nuclear repulsion	-25.99	-25.99	-67.62	-67.62	-332.61	0				
Total	0.34	0.39	0.90	1.05	6.69	0.15				

^aEnergies given here in kcal are the differences between those for the subscripted angle and 0° .

the total for a perpendicular conformation ($\alpha = \beta = 90^\circ$) is 6.3 kcal higher than that for the planar one, which itself, of course, is not the most favorable. Hence, the perpendicular conformation is definitely an unfavorable one on the basis of *ab initio* methods.

Partitioning: Electronic and nuclear components of the torsional energy

The partitioning of the energy into kinetic, nuclear-electron, and electron and nuclear repulsion can yield information as to (1) the nature of the rotational energy surface of NBA (both in the whole molecule and from the model compounds) and (2) any difference between the two basis sets.

The direction of change for the various components of the total energy as revealed by the partitioning (Tables I and II) is the same for both α and β , and the same for both basis sets except for the kinetic energy contribution to β of 24.8° in the 4-31G basis set. The trends are consistent also between NEA and the full molecule. Hence, the fact that the net change upon rotation is stabilizing for α and destabilizing for β is due to a subtle difference in the *balance* of various energy terms. In all cases the nuclear-electron attractive term rises in energy as the nonplanarity increases, presumably due in part to a net lowering conjugation between the bridge and the ring (see below). On the other hand, the energy due to the two repulsive terms decreases. Such a trend is expected from the qualitative picture provided by the electron density maps (Fig. 2). Rotation about the exocyclic bond in both cases increases the distance between the *ortho* ring atoms (carbons and hydrogens) on the one hand and the atoms and lone pair electrons on the bridge on the other hand, thus decreasing the repulsion. For instance, in NEA, the $\text{N}=\text{CH}\cdots\text{H}$ (*ortho*) distance is increased from 1.80 to 2.40 Å as α goes from 0° to 45° , and the repulsive interaction between the electron clouds about these atoms [Fig. 2(a)] would be expected to decrease.

For the conformation equivalent to $\alpha = 90^\circ$ in NEA (Table II), which is 0.4 kcal lower than for the planar conformation, the partitioning reveals that the relative contributions of the various terms differ significantly and the small energy difference is due to the sum of some large changes in the individual terms rather than to any one particular energy component.

Factors determining conformation of NBA

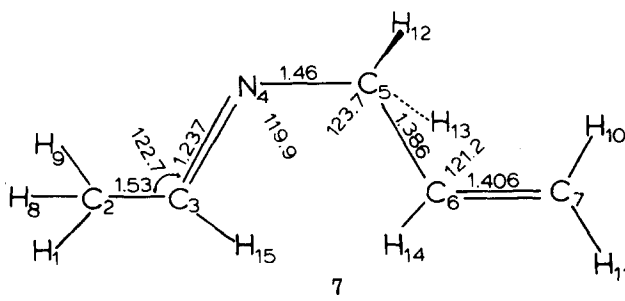
The simplest and most straightforward explanation¹⁷ for the nonplanarity of NBA involves a competition between two principal factors: (1) the interaction of the *ortho* hydrogen on the aniline ring and the hydrogen on the "bridge" carbon E_{NB} which is repulsive in the planar conformation but is reduced with increasing nonplanarity and (2) the π -electron system, itself divisible into two components, including, on the one hand, delocalization between the $-\text{CH}=\text{N}-$ double bond and the aniline phenyl ring E_{DB} , which is maximized for a planar conformation, and, on the other hand, delocalization of the nitrogen lone pair electrons into the aniline ring E_{LP} which is essentially zero for the planar conformation but increases with increasing nonplanarity (where the lone

pair density on the N may interact with the π system of the ring). Burgi and Dunitz¹⁷ carried out an extensive theoretical and experimental study of NBA and related compounds. They calculated the conformation of NBA by using simple Hückel theory together with nonbonded terms to account for steric interactions and successfully accounted for the nonplanar conformation observed in the crystal, which is stabilized over the planar conformation by about 2 kcal. A similar treatment by Tsekhanskii *et al.*¹⁸ led to comparable results.

Details on nonbonded and delocalized π contributions

In principle, a clearer understanding of the nature of the intramolecular interactions underlying the nonplanarity may be obtained from *ab initio* estimates of the relative contributions of the factors which are presumed to determine the conformation of NBA.¹⁷ In particular, we wished to investigate the details of the $\text{N}=\text{CH}\cdots\text{H}$ (*ortho*) nonbonded interaction (E_{NB}) as well as the two delocalization interactions E_{DB} and E_{LP} between the ring system and the exocyclic double bond and the nitrogen lone pair, respectively. In an attempt to isolate and examine these contributions an additional set of model compounds was chosen (or designed) to isolate these factors.

E_{NB} was investigated by considering the differences in energies (as calculated in the 4-31G basis) for a number of conformations of structure 7:



in which both delocalization terms are absent. The geometry of compound 7 was chosen so as to approximate, as closely as possible, the geometry in NBA in the region of the $\text{H}\cdots\text{H}$ interaction in the full molecule and thus does not necessarily represent a true chemical situation.

The results of the calculations on compound 7 are presented in Fig. 3. The energy decreases as a function of rotation about the $\text{N}-\text{CH}$ bond (which is the analog of the N -phenyl bond) and goes through a minimum of approximately -0.40 kcal at $\sim 30^\circ$ torsion angle. This would appear to be a reasonable estimate of the driving force to nonplanarity due to nonbonded $\text{H}\cdots\text{H}$ interactions.

We also attempted to obtain estimates of the two components of the delocalization factor E_{DB} and E_{LP} by carrying out calculations on a number of additional model compounds (8-11) where E_{NB} was not present:

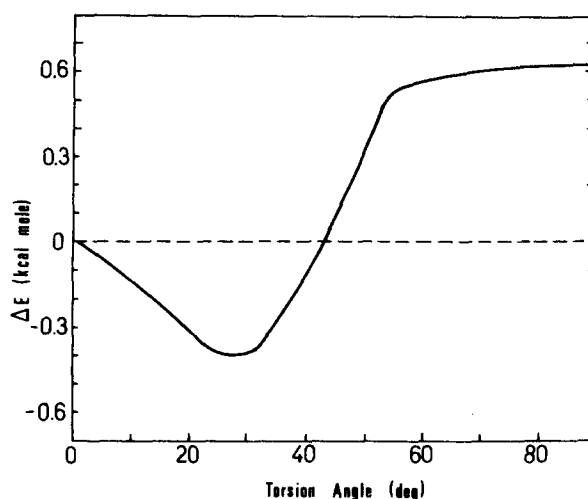
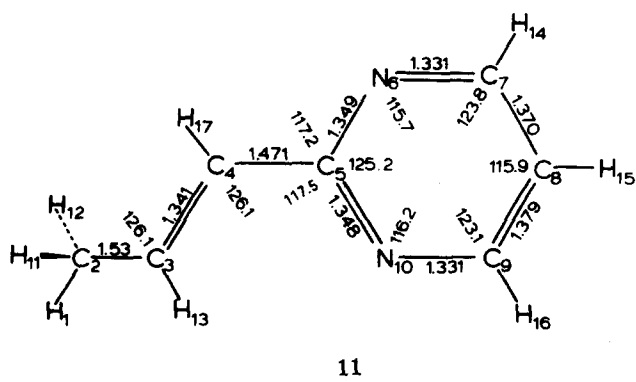
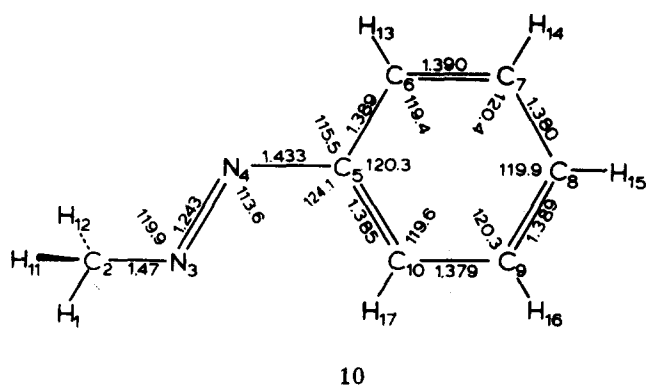
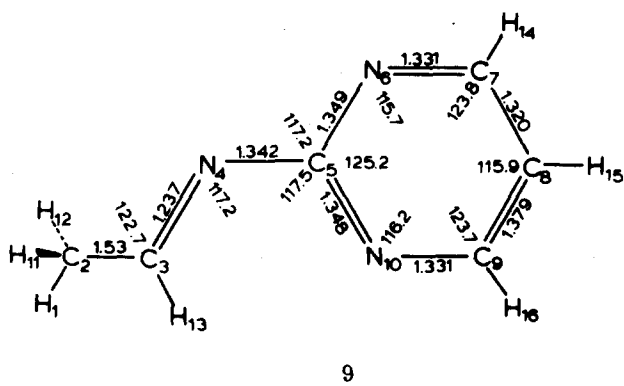
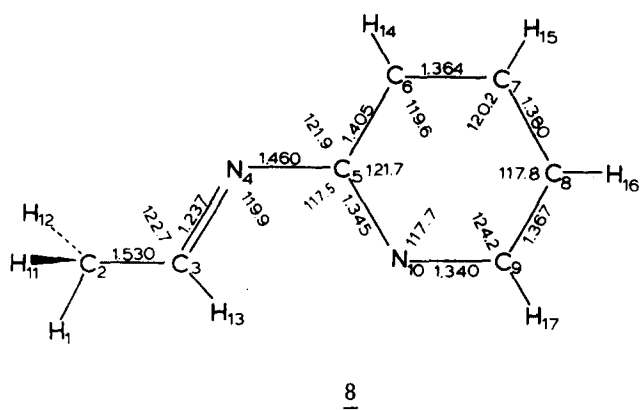


FIG. 3. Estimate of the nonbonded energy E_{NB} as a function of rotation about N_4-C_5 in compound 7. The ordinate represents energy differences between the planar conformation (0°) and nonplanar ones.

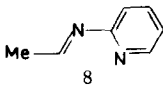
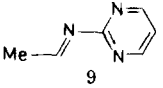
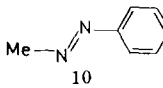
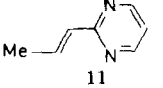
Compounds 8 and 9 were chosen to eliminate the $H \cdots H$ repulsion and isolate the difference in delocalization energies. For these compounds the geometry of the $CH_3-CH=N$ portion of the molecule is identical to that for NEA. Bond lengths and angles for the pyridine ring in compound 8 were taken from the structure of 2-aminopyridine²¹ while those for the pyrimidine ring in compound 9 were taken from 2-aminopyrimidine.²² Assuming sp^2 hybridization on the bridge nitrogen in compound 8, any delocalization would be between the double bond and the ring, at a torsion angle of 0° about the N-phenyl bond, while at 90° delocalization would be between the nitrogen lone pair and the ring. Hence, the energy difference between 0° and 90° is $E_{DB} - E_{LP}$. Compound 9 serves as a check on the perturbation which results from the inclusion of nitrogen in the ring.

E_{NB} is also eliminated by employing compound **10** where the phenyl ring is retained but the bridge carbon has been replaced by a nitrogen. The geometry for this molecule was taken from the crystal structure of azobenzene.^{3(a)}

Based on the same set of assumptions E_{DB} may be estimated from compound 11, where E_{LP} and E_{NB} have been essentially eliminated. The geometry about $CH=CH$ was taken from the structure of *trans*-stilbene^{4(a)} and that of the pyrimidine ring from Ref. 22.

The results of these calculations are presented in Table III. There is quite a wide variation among the values obtained for $E_{LF} - E_{DB}$, and indeed the range of values is somewhat larger than the energy differences in the known conformations of NBA. Except for compound 9 the energy increases on going from $\alpha = 0^\circ$ to $\alpha = 45^\circ$ and we can attribute the decrease in energy in that compound to a relaxation of the repulsion between nitrogen lone pair electrons on the double bond and those from one nitrogen on the ring. However, the values obtained provide an estimate of the magnitudes of the contributions to the total energy, and bear out the correctness of the qualitative model of the competition of a num-

TABLE III. Summary of *ab initio* calculations in model compounds 8–11 (4-31G basis set).^a

	 8		 9		 10		 11	
Energy Component	$\alpha = 90^\circ$ ($E_{LP} - E_{DB}$)	$\alpha = 45^\circ$	$\alpha = 90^\circ$ ($E_{LP} - E_{DB}$)	$\alpha = 45^\circ$	$\alpha = 90^\circ$ ($E_{LP} - E_{DB}$)	$\alpha = 45^\circ$	$\alpha = 90^\circ$ E_{DB}	$\alpha = 45^\circ$
Kinetic energy	-18.57	-12.34	-46.37	-32.14	-15.43	-8.98	-6.19	1.39
Nuclear-electron	1501.56	1169.30	1511.74	776.54	383.84	-952.60	953.60	476.20
Electron repulsion	-802.86	-665.37	-782.27	-400.45	-225.00	485.55	-496.33	-246.96
Nuclear repulsion	-675.19	-486.36	-682.22	-345.30	-136.29	507.75	-454.45	-226.34
Total	4.94	5.23	0.88	-1.33	7.11	4.83	9.01	4.33

^aQuantities are in kcal/mol and are the differences between energy for either the perpendicular conformation ($\alpha = 90^\circ$) or ($\alpha = 45^\circ$) and the planar conformation ($\alpha = 0^\circ$).

ber of factors in determining the conformation of NBA. Based on the values obtained for compounds 8 and 10 we can roughly estimate $E_{LP} - E_{DB}$ to be ~ 6 kcal/mol while the E_{DB} contribution estimated from compound 11 (and to some extent from compound 6) is somewhat larger. This does suggest that E_{LP} contributes to the stabilization energy at 90° and that E_{DB} stabilizes the planar conformation while E_{NB} destabilizes it. This is consistent with the fact, noted above, that $E_{\alpha=90^\circ}$ for NBA is 0.4 kcal lower than $E_{\alpha=0^\circ}$ (with β fixed). A more quantitative estimate of the relative contribution of these factors is complicated in all these model compounds by the presence of $1 \cdots 4$ interactions which differ throughout the series. As particularly evidenced by compound 9, substitution of nitrogen for carbon in the ring system with the addition of a lone pair of electrons capable of interacting with the double bond at nonzero torsion angle is an additional complicating factor.

Conformational charge distribution and its conformational dependence

The partial charges on the atoms in NEA resulting from a population analysis using the 4-31G basis set are

TABLE IV. Partial charges (e) on compound 5 as a function of exocyclic angle α (4-31G basis set).

Atom	$\alpha (^\circ)$				
	0.0	24.8	45.0	55.0	90.0
C ₂	-0.470	-0.472	-0.475	-0.476	-0.476
C ₃	-0.095	0.089	0.084	0.084	0.086
N ₄	-0.535	-0.522	-0.505	-0.499	-0.490
C ₅	0.149	0.145	0.137	0.132	0.127
C ₆	-0.170	-0.171	-0.174	-0.174	-0.182
C ₇	-0.192	-0.190	-0.188	-0.186	-0.181
C ₈	-0.190	-0.191	-0.194	-0.195	-0.198
C ₉	-0.184	-0.184	-0.183	-0.182	-0.180
C ₁₀	-0.190	-0.189	-0.188	-0.188	-0.189
H ₁	0.155	0.155	0.156	0.157	0.157
H ₂	0.190	0.190	0.190	0.191	0.191
H ₁₂	0.190	0.191	0.191	0.191	0.191
H ₁₃	0.163	0.164	0.165	0.166	0.168
H ₁₄	0.214	0.213	0.211	0.209	0.203
H ₁₅	0.190	0.190	0.190	0.190	0.190
H ₁₆	0.196	0.196	0.195	0.195	0.194
H ₁₇	0.194	0.194	0.194	0.194	0.195
H ₁₈	0.196	0.193	0.192	0.193	0.198

given in Table IV. The charge on the nitrogen decreases while that on the ring increases with increasing α , reaching a maximum at $\alpha = 90^\circ$, indicating a movement of charge with increasing nonplanarity. There is a similar though less pronounced effect for the entire NBA molecule (Fig. 4). The difference in magnitude between the two molecules is due in part to the difference in basis sets,¹⁶ since the extended basis set is known to overemphasize the magnitudes of atomic partial charges. Nevertheless, these results do indicate that there is some delocalization from the lone pair on the nitrogen into the aniline ring. For the full NBA molecule the *net* charge on the ring including H's is decreased with increasing torsion angle, from a value of 0.112e for the planar conformation to 0.103e for $\alpha = 45^\circ$, $\beta = 0$. For NEA a similar trend is observed which is consistent with the dominant role of E_{DB} compared to E_{LP} . In both NBA and NEA the negative charge increases at the *ortho* and *para* positions and decreases in the *meta* position. The charge on the benzylidene ring in the full molecule is essentially unaffected by rotations about the N-phenyl bond. One possible reason for the failure of the semiempirical methods for systems of this type is that in general the role of delocalization is overemphasized in comparison with other effects. It appears in the *ab initio* treatment as well, as it should, but does not dominate to the extent of leading to a prediction of $\alpha = \beta = 90^\circ$ for the most stable conformation of NBA.

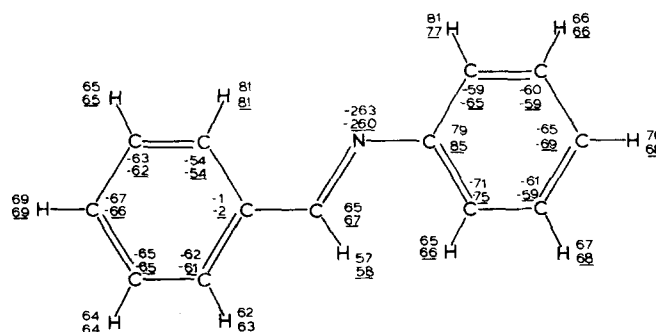


FIG. 4. Electronic charges ($\times 10^3$) obtained by population analysis of STO-4G basis set calculations on NBA. For each atom the upper figure represents the charge for a planar molecule ($\alpha = \beta = 0^\circ$); while the lower (underscored) figure represents that for the minimal energy molecular conformation ($\alpha = 45^\circ$, $\beta = 0^\circ$).

Basis set dependence of the results

In all cases where both were employed the two basis sets yield the same general trends and predict the same geometry, suggesting that good estimates of conformational energetics may be obtained from minimal basis set calculations in this case. For model compound **5** the difference between total energy for the two basis sets for the minimum configuration is -0.22 kcal, with the extended basis set yielding the greater stabilization energy. The partitioning indicates that the electron repulsion energy is higher for the extended basis set while the nuclear-electron attraction results in a significant stabilizing effect.

Additivity of energies for model compounds

We are now in a position to check the validity of NEA and NMBI as models for the conformational energetics in NBA. Using the minimal basis set results for NEA and NMBI and assuming the additivity of the energy differences obtained from them, we obtain a net stabilization of the minimum energy conformation $\alpha = 45^\circ$, $\beta = 0^\circ$, favored over the planar one by 1.99 kcal. Comparison of these results with those obtained for the full molecule (Table I) suggests that the use of the model compounds along with the assumption of additivity gives a reasonable approximation but overestimates the energy of stabilization by about 30%.

The validity of the choice of compounds **5** and **6** is also suggested by the additivity of the partitioned components of the total energy. For instance, the sums of the components for 24.8° for compounds **5** and **6** closely approximate the values obtained for the full molecule when $\alpha = -\beta = 24.8^\circ$. In other words, the individual contributions to the total energy are essentially the same for the model compounds as for the full molecule. In view of the fact that the 4-31G contributions for the model compounds closely parallel the STO-4G entries, the extrapolation to the full molecule seems justified.

The two basis sets give results favoring the nonplanar conformation $\alpha = -\beta = 24.8^\circ$ found in the orthorhombic crystal of DCBA over the planar conformation (found in the triclinic structure) by approximately half a kilocalorie (0.47 kcal in the STO-4G and 0.44 kcal in the 4-31G). Again, the stabilization is consistent with the full NBA molecule calculation with the minimal basis set, but the stabilization energy calculated for NBA is less than half that obtained by summing the results for the model compounds. We note that for the $\alpha = -\beta = 24.8^\circ$ the 4-31G calculations for the model compounds yield essentially the same stabilization energy as those for the minimal basis set.

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