CNDO Calculations on Benzylideneaniline[‡]

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CNDO/2 calculations lead to a conformation for *trans-N*-ben-
zylideneaniline in agreement with most of the previous theoretical
and experimental results. The electron exicitation spectrum calcu-
lated after optimization of the bond lengths by the CNDOS method
accords well with the experimental spectrum in respect of the
position of the electron transitions.

INTRODUCTION

trans-N-Benzylideneaniline differs from the isoelectronic and substantially
planar *trans*-stilbene and *trans*-azobenzene in some physicochemical propert-
ies[1,2], e. g. different UV spectrum, lack of luminescence, low basicity, and an
unstable *cis*-isomer. These unusual properties of benzylideneaniline have been
ascribed to a molecular geometry that differs from those of *trans*-stilbene and
trans-azobenzene (Table I): either a widening of bond angle β or, more, often,
a non-planar conformation is proposed. The possible causes of this are steric
interaction of the olefinic hydrogen with the nearest hydrogen atom of the
N-phenyl group and perhaps an nπ-interaction of the lone electron pair with
the *N*-phenyl ring.

In the crystalline state the *N*-phenyl ring is twisted by 55⁰ out of the
molecular plane and the C-phenyl ring is twisted by 10⁰ in the opposite
direction[13]. In solution a marked change in conformation may occur owing to
absence of the lattice forces. However, the UV spectrum of benzylideneaniline
greatly resembles the reflection spectrum of a powdered mixture of benzylidene-
aniline and barium sulphate[7]. In solution, therefore, a conformation similar
to that in the crystalline state is to be expected. Nevertheless, as follows from
Table I, controversy remains about the structure of the molecule as a result of
the theoretical investigations. Since, furthermore, no theoretical study has
hitherto satisfactorily reproduced the UV absorption spectrum of benzylidene-
aniline[2,4,11,12,16,18], we have carried out new quantum-mechanical calculations.

RESULTS AND DISCUSSION

We used the CNDO/2 method[20] for calculating the properties of the ground
state. We first calculated the energy in dependence on the angles Θ and γ.

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TABLE I

Collation of the Previous Theoretical and Experimental Data for the Conformation of trans-N-Benzylideneaniline.
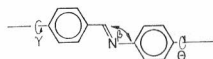
| Method | | Conformation | | Year | Ref |
		$\Theta/\deg$	$\gamma/\deg$		
UV + Melting-point diagram	p	0	0 $\beta=180$	1942	3
EHMO	c	0	0 $\beta=156$	1969	4
UV	p	90	0	1956, 1960, 1968	5,6 1
EHMO	c	90	0	1971	7
CNDO/2	c	90	53	1971	8
MINDO/3	c	90	90	1976	9
UV	p	<90	0	1962	10
HMO	e	<90	0	1963, 1965	11,12
HMO + Nonbonded interactions	e	40—60	0	1967	2
Atropoisomerism	e	<90	0	1967	2
UV	e	55	0	1967	2
X-ray crystal analyses	o	55	10	1970	13
NMR	e	⩽45	0	1971	14
NMR + HMO	e	42—50	0	1971	15
HMO + Nonbonded interactions	e	40	0	1971	7
UV + SCF-CI	e	<55	0	1972	16
Photoelectron spectra + HMO	c	46	0	1974	17
Photoelectron spectra	e	36	0	1976	9
PCILO	c	36	0	1977	19

p: postulated, c: calculated, o: observed, e: estimated

For this purpose we twisted the N- and the C-phenyl rings by 5° steps and for each of the resulting angular positions carried out a CNDO/2 calculation with Pople-Segal parametrization[20]. The result is shown in Figure 1. Intersecting curves through the energy surfaces for angles above 180° to 360° for the N-phenyl ring were not calculated but were taken over from the values of 0° to 180°. The energy minimum lies at $\Theta = 40°$ and $\gamma = 175°$ and $\Theta = 140°$ and $\gamma = 5°$. For $\Theta = 140°$ and $\gamma = 175°$ and $\Theta = 40°$ and $\gamma = 5°$ the value obtained is only 0.1 kJ/mol higher. In contrast to the earlier CNDO/2 calculations by Warren et al.[8] ($\Theta = 90°$, $\gamma = 53°$), these values correspond more closely to the previous experimental and theoretical results. Warren et al. obtained 20 kJ/mol for the rotation barrier of the N-phenyl ring and 1.7 kJ/mol for that of the C-phenyl ring. According to our calculations two barriers exist for the N-phenyl ring: ca. 1.7 kJ/mol at about the 90° position and ca. 0.9 kJ/mol around the 0° position. 5.0 kJ/mol is obtained for the C-phenyl ring.

The values of the rotation barriers are nevertheless not wholly reliable, since the calculated total energies for the various positions of the angles Θ and γ depend on the geometry used[21]; indeed, it is possible that other angles
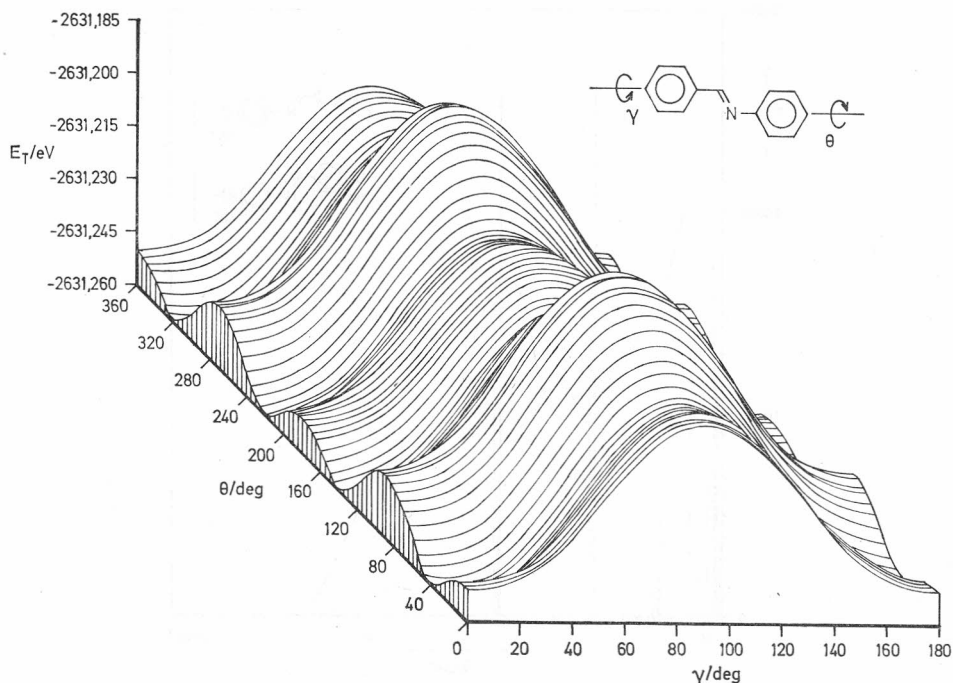
Figure 1. Total energy E_T of *trans-N*-benzylideneaniline as a function of the angles Θ and γ.

would result for the energy minimum. For a more accurate calculation it would be necessary to carry out an optimization of the geometry for each of the calculated angle positions, for even small changes in the geometry could lead to significant changes in the energy surface[21]. Such calculations would be very troublesome in the case of the benzylideneaniline because of the large number of parameters to be optimized.

The fact that the conformation determined by us accords better than that determined by Warren et al. with most of the previous experimental and theoretical results is also shown on calculation of the electron excitation spectrum by Del Bene and Jaffé's CNDO/S method[22] (approximation for the two-centre Coulomb integrals according to Nishimoto and Mataga's method). The most stable conformation calculated by Warren et al. leads by the CNDO/S method to approximate agreement with the gas spectrum (Figure 2), but this could be fortuitous since a shift to higher wave numbers must occur because of the loss of conjugation with increasing twist.

Furthermore, although the CNDO/2 calculations are valid for an isolated molecule, the electron excitation spectrum should agree with the solution spectrum rather than with the gas spectrum; this is because in the CNDO/S method the theoretical spectra are made to accord largely with the solution spectra through an empirical factor kappa that weights the resonance integrals of the σ- and the π-electrons differently. The conformation determined by us leads to an approximate agreement with the solution-spectrum (Figure 2).
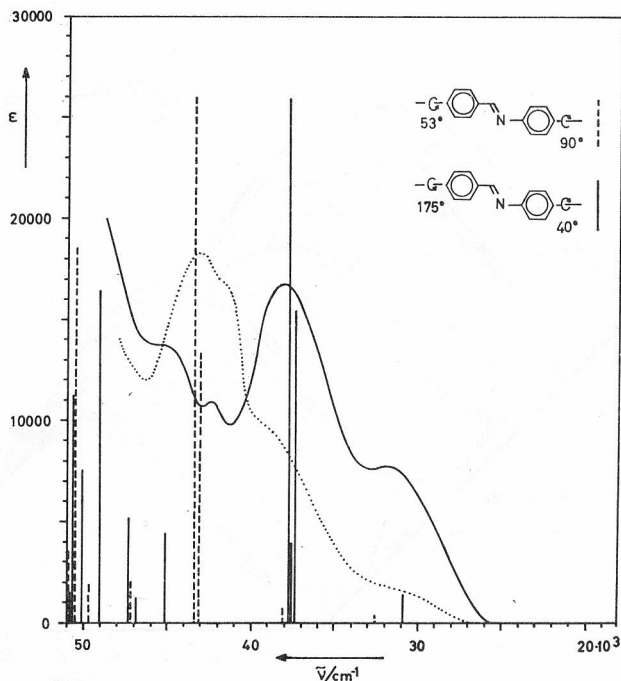
Figure 2. Electron excitation spectrum of *trans*-N-benzylideneaniline in the gas phase (. . . . .)
and in cyclohexane (———). The vertical lines show the positions of the calculated electron
transitions for the two conformations (Warren et al.[8] and present work). Scale: $\varepsilon = 5000 \cong$ oscillator strength = 0.1.

To obtain better agreement we have optimized with respect to bond lengths
the most stable conformation ($\Theta = 40^0$, $\gamma = 175^0$) obtained by unoptimized
geometry. The geometrical optimization depends on the method of steepest
descent for the minimization of the calculated energy surface for the molecule.
In Table II the bond lengths of the geometry originally assumed are compared
with those obtained after optimization. The originally assumed geometry
resulted from earlier calculations on azostilbenes with these bound-distances[23].
There was a good correlation between the calculated and experimental electron
excitation spectra.

TABLE II

*Bond Lengths before and after Optimization for the Calculated most Stable
Conformation of* trans-N-*Benzylideneaniline* ($\Theta = 40^0$, $\gamma = 175^0$)

Bond	Assumed Bond Distances Å	Bond Distances after Geometrical Optimization Å
Ph—C	1.54	1.44
C=N	1.32	1.30
Ph—N	1.48	1.40
All C—H	1.08	1.12
All ring C—C	1.39	1.38—1.40
	All angles 120⁰	

For the dipole moment we obtain before optimization a value of 1.55 D and after optimization a value of 1.69 D. Both values agree with the experimental value of 1.57—1.60 D[24] better than does that obtained by Warren et al. (1.83 D).

The result of the geometrical optimization is a molecule more stable by 95 kJ/mol. Clearly, the geometrical optimization has an effect on the electron excitation spectrum calculated by the CNDO/S method (Figure 3). The agreement with the experimental spectrum is better than in the case of the unoptimized geometry. We now also find a transition at about 42 500 cm⁻¹, in approximate agreement with experiment, so that the agreement is satisfactory except for the intense calculated transitions around 37 500 cm⁻¹.

We calculated the energy with optimized geometry in dependence on the angles Θ and γ to find out the effect of optimized bound-distance on our results. Comparable to the results of Figure 1 the molecule is less stable by 96 kJ/mol while other data are only little different from the originally ones. The energy minimum lies now at $\Theta = 40^0$ and $\gamma = 160^0$ and $\Theta = 40^0$ and $\gamma = 20^6$. For $\Theta = 140^0$ and $\gamma = 160^0$ and $\Theta = 40^0$ and $\gamma = 20^0$ the value obtained is only 0.8 kJ/mol higher. The rotation barrier of the 1 N-phenyl ring is now 2.4 kJ/mol (about the 90⁰ position) and 1.9 kJ/mol (about the 0⁰ position). 5.6 kJ/mol is obtained for the C-phenyl ring and for the dipole moment, we obtain a value of 1.63 D. The calculated electron excitation spectra by CNDO/S method are by far identical with the Figure 3.

Our attempt to optimize the angle β led to the divergent result of 90⁰. Presumably the approximations in the CNDO/2 method are too severe to reproduce correctly the small energy differences occurring here.
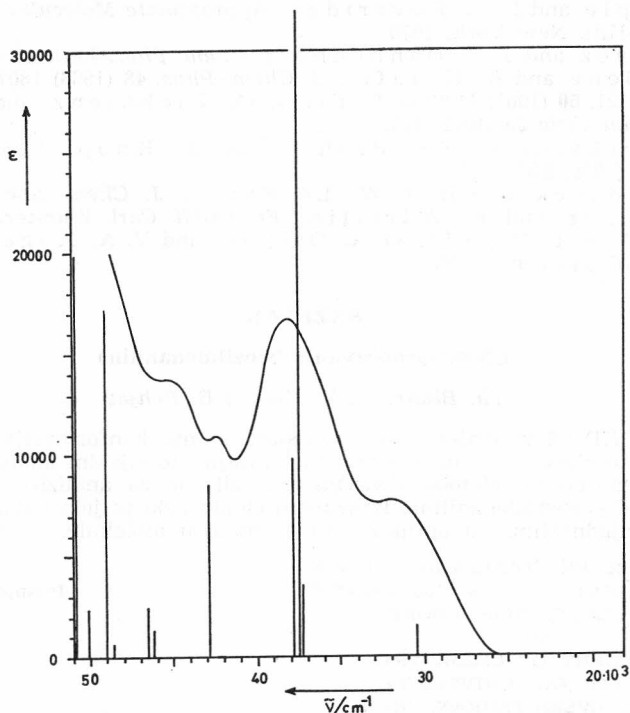

Figure 3. Calculated electron transitions for the most stable conformation determined for trans-N-benzylideneaniline after optimization of the bond lengths.

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SAŽETAK

CNDO-proučavanje benzilidenanilina

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Metoda CNDO/2 upotrijebljena je za predviđanje konformacije *trans-N*-benzilidenanilina. Teorijski je račun u slaganju s ranijim teorijskim analizama i eksperimentalnim rezultatima. Metoda CNDO/S poslužila je za analiziranje elektronskog spektra *trans-N*-benzilidenanilina. Izračunani elektronski prijelazi slažu se s eksperimentalnim vrijednostima za optimiziranu geometriju molekule.

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