

MBBA 와 EBBA 의 합성 NMR 스펙트럼과 분자궤도함수론적 연구

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The Synthesis, NMR Spectrum and MO Theoretical Studies on MBBA and EBBA

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요약. 합성한 MBBA, 와 EBBA 의 NMR spectrum 의 분석결과로 *N*-(*p*-methoxy benzylidene)-*p*-*n*-butylaniline(MBBA) 와 *N*-(*p*-ethoxy benzylidene)-*p*-*n*-butylaniline(EBBA) 분자내의 *p*-*n*-butylaniline 의 벤젠핵과 분자내의 다른 이중결합 사이에 'conjugation 이 일어나고 있지 않음을 발견 하였으며 이 벤젠핵은 분자 방면으로부터 이탈되어 있다는 결론과 분자궤도 계산결과 벤젠기가 평면에서 30도 이탈되어 있을 때 minimum energy conformation 을 지님을 알았고 이는 NMR 분석결과와 잘 일치하였다.

Abstract. By means of NMR spectrum analysis of the synthesized MBBA and EBBA, it has been found that benzene rings of *p*-*n*-butylaniline in both MBBA and EBBA molecules do not conjugate with the central double bond and the benzene ring is twisted from molecular plane of *N*-(*p*-methoxy or ethoxy benzylidene) group. And as a result of MO studies, the minimum energy conformation is found for the conformation of 30° twisted angle. One sees reasonable agreement between theory and experiment.

Introduction

Scientific researches on the liquid crystalline materials have been developed greatly during the last several years.⁽¹⁾ Of particular importance to the organic chemist is the relationship between chemical structure and mesomorphic properties of organic compounds.

Since most of substances, which exhibit nematic mesophases, have melting points above 100°C and are unstable to moisture, acids or bases, and so forth, many chemists have studied to obtain substances which exhibit nematic mesophases at room temperature and simultaneously, have long-term stability under ambient condition.

It is well known that molecules, which possess a high degree of symmetry pack well in

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the solid phases, exhibit relatively high melting point. This rule has been extended to apply in the liquid crystal as well as in the solid phases, and we hypothesized that the compound which have nonplanar in the molecular structure will exhibit significantly lower melting points than their planar counterparts. On this basis, the conformation of MBBA and EBBA which exhibit nematic mesophases at room temperature is studied by NMR and MO theory. As expected, the benzene rings in both MBBA and EBBA molecules are twisted out of coplanarity in order to relieve steric crowding about the central double bond. Our results may be useful to design the molecular structure which exhibit nematic mesophase at room temperature and to synthesize those substances.

stirred liquid has been cooled to 5 °C, 14.9 g (0.1 M) of *p*-butylaniline** was added slowly without allowing the temperature to rise above 15 °C during about half hours, and the stirring was continued for three hours as room temperature. EBBA had been distilled from the mixture at 2 mm pressure. EBBA distilled at 224~226 °C, yield 22.5 g (80 %), m. p 35~36 °C.

Anal. C₁₉H₂₃NO Calc. C : 81.1 % H : 8.2 %
N : 4.98 %
Found. C : 80.7 % H : 8.3 %
N : 5.00 %

With the use of similar method mentioned, *p*-methoxy benzylidene-*p*-butylaniline (MBBA) was prepared.

Calculation

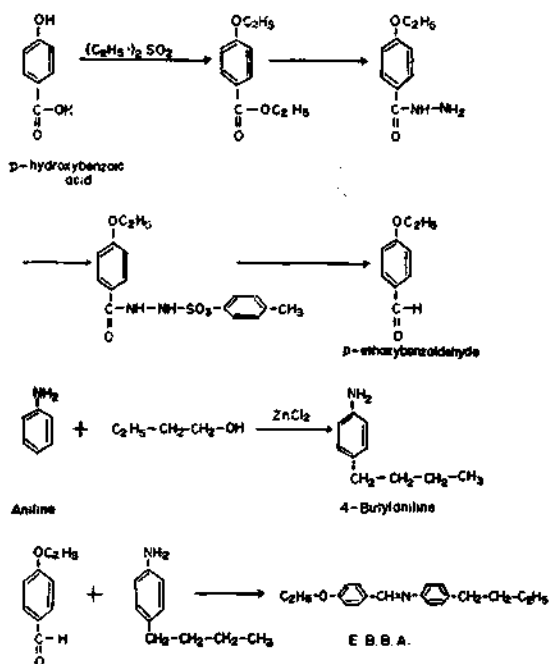
In previous studies⁴⁻⁸ we have successfully applied a semiempirical molecular orbital theory to predict molecular conformations. The method we have used is known as extended Hückel theory developed by Hoffmann⁹. The expansion of a molecular orbital as a linear combination of atomic orbitals yields

$$\Psi_i = \sum C_{ij} \phi_j$$

upon minimizing the total energy, a set of Hückel equations arises

$$\sum_{j=1}^n (H_{ij} - ES_{ij}) C_{ij} = 0 \quad (i=1, 2, \dots, n)$$

where Ψ_i is the molecular orbital wave function, H , the Hamiltonian operator, E , the energy, S , the overlap integral, and C the orbital coefficient. The calculations are performed for the valence electron in S and P orbitals



*Synthesis of *p*-ethoxy benzaldehyde

This material is synthesized by McFadyen Stevens method.²

**Synthesis of *p*-butylaniline³

This material is synthesized through Friedel crafts method starting with aniline and *n*-butylalcohol. As a catalysis ZnCl₂ is used.

using Slater orbitals as a basis set. The input parameters consist of the Slater exponent and the Coulomb integral, approximated as the valence state ionization potential. All overlap integrals are considered. The resonance integrals are approximated by the equation.

$$H_{ij} = 0.5 K (H_{ii} + H_{jj}) S_{ij}$$

with K set at 1.75 the value preferred by Hoffmann. The total electronic energy is computed to be the sum of the doubly occupied molecular orbitals,

$$\sum E_t = 2 \sum E_i$$

Since all overlap integrals and all nonbonded interactions are explicitly considered, the computed total energy E_t is sensitive to the geometry of the molecule. Thus by varying the geometry and calculating the total energy, E_t for each, the minimum energy is found, which corresponds to the preferred conformation. It is therefore necessary to include the three dimensional coordinates of each atom in the conformation selected for calculation. These are derived using a vector program which locates each atom in space in Cartesian coordinates. The bond lengths used were C-C=1.54 C-O=1.42 C-H=1.09 C=C=1.40 C-CN=1.45 CN-H=1.08 C-N=1.31, all in angstroms.

All bond angles were $\angle \text{COC} = 115^\circ$ $\angle \text{CCN} = 125^\circ$ $\angle \text{CNC} = 125^\circ$, assumed tetrahedral on the alkyl group and 120° between each atom in benzene ring.

The input parameters are listed in Table 1.

Results and Discussion

To evaluate the conformation of *N-p*-methoxy (or *p*-ethoxy) benzylidene-*p-n*-butylaniline, we assume that the substituents in para positions will not grossly affect the configuration of benzene rings and of the linkage group¹²

and have calculated energy to rotate benzene ring about N-C bond axis between nitrogen

of $\text{R}_3\text{O}-\text{C}_6\text{H}_5-\text{CH}=\text{N}-\text{C}_6\text{H}_5$ ($\text{R}=\text{CH}_3$ or C_2H_5) and phenyl radical, respectively, at the coplanar, 15° angle, 30° angle and 45° angle. The energy minimum value have been found at 30° angle as shown in Table 2.

The result indicate that the benzene ring in both MBBA and EBBA molecules are twisted out of the coplanarity in order to relieve steric hindrance about the central double bond and does not conjugate with the central double bond (see Fig. 1).

For the confirmation of our molecular orbital prediction by NMR analysis, we have investigate the NMR (100 M cps) spectrum of *p*-ethoxy benzaldehyde, *p*-butylaniline and *p*-methoxybenzylidene *p-n*-butylaniline in carbon tetrachloride with TMS as internal standard. The spectrum of each molecules have shown

Table 1. Coulomb integrals^{10,11}

Electron	Value (eV)	Electron	Value (eV)
N 2s	-26.00	O 2p	-17.76
N 2p	-13.40	C 3s	-21.40
O 2s	-35.30	C 2p	-aa.40

Slater exponents

Atom	Value	Atom	Value
H	1.000	N	1.950
C	1.625	O	2.275

Table 2. The energy minimum value

Angle (degree)	Energy (eV)	Energy (Kcal/mol) barrier
0°	-1453.90	13.69
15°	-1454.23	5.98
30°	-1454.49	0
45°	-1454.13	7.25

that the splitting of phenyl proton in *p*-ethoxy benzaldehyde exhibit at 2.37 τ and 3.17 τ as a multiple peak as shown in Fig. 2.

And phenyl protons in *p*-butylaniline also give splitting at 3.17 τ and 3.60 τ in Fig. 2.

In the case of EBBA the phenyl protons with ethoxy group at the para position give splittings at 2.36 τ and 3.26 τ .

However, phenyl protons with butyl group give singlet at 2.98 τ as shown in Fig. 4.

These result are consistent with the hypothesis relating melting point and molecular nonplanarity which the induced steric repulsions caused the benzene rings to twist out of coplanarity. Nonplanarity of MBBA and EBBA molecules by our calculation indicate 30° torsion angle.

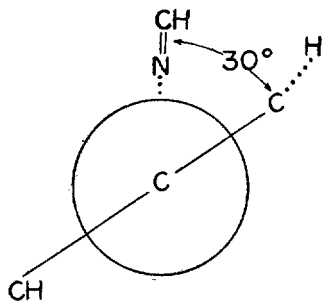


Fig. 1. Conformation predicted for *N*-(*p*-methoxy (ethoxy) benzylidene)-*p*-aniline viewed down the benzene ring has 30° torsion angle from *N*-(*p*-methoxy (ethoxy) benzylidene) group.

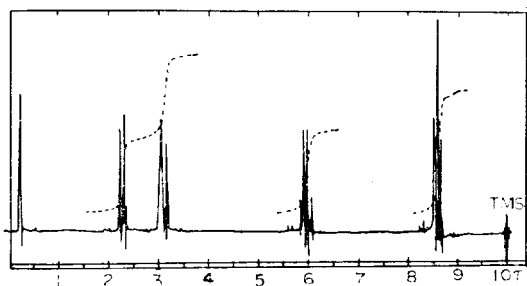


Fig. 2. NMR(100 M cps) spectrum of *p*-ethoxybenzaldehyde in carbon tetrachloride with TMS as internal standard

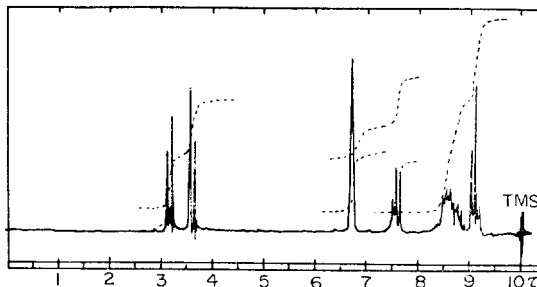


Fig. 3. NMR(100 M cps) spectrum of *p*-butylaniline in CCl₄ with TMS as internal standard.

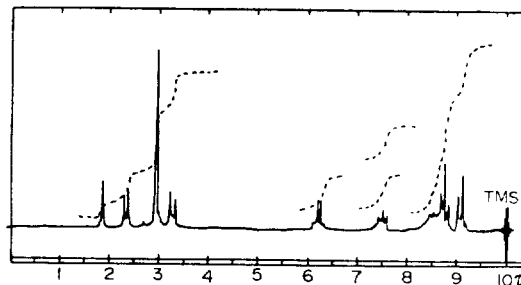


Fig. 4. NMR(100 M cps) spectrum of EBBA in CCl₄ with TMS as internal standard

By means of NMR spectrum analysis shown in Fig. 2~ 4, it has been found that *p*-butyl phenyl ring do not conjugate with the double bond in schiff's base, and also, the phenyl ring substituted with *p*-butyl group is twisted from molecular plane of *p*-alkoxy-benzylidene group. In case substituted phenyl proton shows singlet peak, one sees that either the substituted radical does not conjugate with phenyl radical as found in toluene molecule, or due to steric effect, two phenyl proton in different plane does not conjugate each other as *cis* stilben molecule does. However, in case of *trans* stilben, phenyl radicals located at the both side of vinyl radical are in same vinyl radical plane. And it is expected to have conjugation which provide multiple splitting in NMR spectrum. One sees that our MO calculated values are in good agreements with NMR data.

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