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Internal Rotation of N-(*p*-methoxybenzylidene)-*p*-*n*-butylaniline (MBBA) and Benzylidene-aniline (BA)

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The UV absorption spectrum of gaseous MBBA was observed at 110°C. The electronic structures of BA and MBBA were calculated as a function of the twist angle of aniline ring out of the C=N—C plane by means of the CNDO/S + CI method. The twist angle in MBBA was estimated as 52.0° in nematic, 66.3° in metastable solid, and either 44.4° or 82.7° in stable solid using the calculated and observed electronic spectra and the observed Raman scattering frequency. A potential energy curve for the internal rotation in MBBA in solid states was proposed to give a reasonable interpretation of the experimental data and the calculated results.

INTRODUCTION

The polymorphism in solid N-(*p*-methoxybenzylidene)-*p*-*n*-butylaniline (MBBA) was evidenced previously by the calorimetric measurements.[1,2] A glass transition and an irreversible transition with a gradual heat evolution were observed for several metastable solid states (intermediate states). So far, the difference between the melting entropies of the stable and metastable solids of MBBA has been interpreted as being due to the motions of the methoxy and *n*-butyl "tails" of the molecule.[3] There is no available information on the crystal structures for the solid states. Previously the Raman scattering[4,5] and UV absorption studies[6] were reported for the various states of MBBA. For gaseous state, an UV absorption spectrum is reported in this paper.

On the other hand, many papers have been published on the absorption spectra,[7] PES[8] and MO calculation[9–11] of benzylideneaniline (BA), parent compound of MBBA, concerning the nonplanarity problem of the molecule.

By an X-ray analysis of BA crystal it was found that the aniline ring is twisted out of the C=N—C plane by 55.2°.[12] The absorption spectra of BA and MBBA in various states are very similar to each other. They have two characteristic absorption bands in the region of 250–350 nm.

A reasonable interpretation of the observed results for MBBA and BA was attempted here by taking into account twists of aniline (A) and benzyliden (B) rings out of the C=N—C plane and by calculating the electronic spectra as a function of the twist angle by means of the CNDO/S + CI method.[13]

ELECTRONIC SPECTRUM OF GASEOUS MBBA

MBBA in a nematic state was introduced into a gas cell of 10 cm length and inner air was evacuated by a vacuum pump. At room temperature the vapor pressure of MBBA is too low to be detected by UV absorption method. Therefore, the gas cell was heated gradually by two blowers to about 110°C avoiding condensation of MBBA vapour on the surfaces of the windows. A chromel-*p*-constantan thermocouple was tied to the center of the glass body and a precision digital meter (Yokogawa Electric Works. Ltd. Type 2501) was used to measure the emf of the thermocouple. Cary 14 M spectrophotometer was used to measure the absorption spectra of gaseous MBBA. The obtained result is shown in Figure 1.

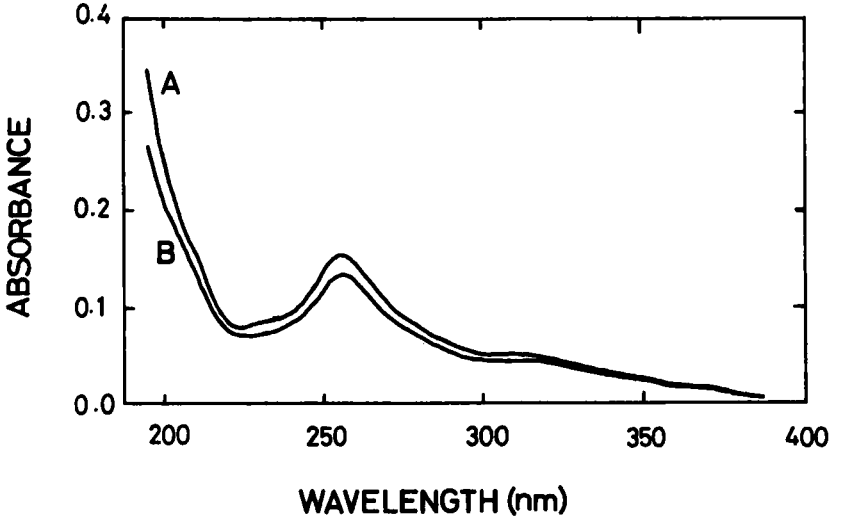

FIGURE 1 UV absorption spectra of MBBA in vapor phase: (A) 111.6–112.8C, (B) 109.5–111.0°C.

This spectrum shows two peaks at 256 nm and 320 nm, the former is strong and the latter is very weak. This is different from the spectra of MBBA in the isotropic liquid, dilute solution and nematic states. These spectra are similar to each other exhibiting three strong absorption peaks at 200 nm, 280 nm and 320 nm as was reported previously.[6] These spectral variations may well be explained by taking into account a conformational change around the C=N—C plane of MBBA as has been done in the case of BA. The CNDO/S + CI calculations of MBBA and BA have been performed to make the above situation clearer.

CNDO/S + CI CALCULATION

It is very erroneous to determine a stable conformation of relatively large molecule such as BA using total energy calculated by the traditional MO method. The resultant total energy is largely dependent on the parameters and geometry of the molecule employed in the calculation.[11] Minkin *et al.*[9] calculated the electronic structure of BA by means of ASMO CI Pariser-Parr-Pople's method, but *n*-orbital was not taken into consideration and the $n\pi^*$ transition which is essential in this case was absent in their calculated spectrum. We employed the CNDO/S + CI method including all valence electrons and applied it to the calculation of electronic spectra of BA and MBBA to analyse the observed results.

The most probable and effective conformational change on the electronic state of BA or MBBA may be the twist motion of A ring around the single C—N bond (this angle is denoted by θ) or the twist motion of B ring around the single C—C bond (this angle is denoted by ϕ). The CNDO/S + CI calculation may be appropriate to reproduce the change of the electronic spectra of MBBA or BA due to the above mentioned conformational changes, because these compounds have a non-bonded electron pair on the N atom of the azomethin group and $n\pi$ interaction plays a very important role in this problem.

The molecular geometries employed here are listed in Table I, and the conformational parameters are shown in Figure 2. Figure 2 illustrates the planar conformation of MBBA used in this calculation and it has a C_s symmetry. The *p*-methoxybenzylidene and *n*-buthyl groups are thought to be coplanar with the C=N—C plane against the twist of A ring.

The Nishimoto-Mataga potential was adopted for the Coulomb repulsion integrals and an average of the experimental values for 2*s* and 2*p* electrons were used to the one-center Coulomb integral as follows; $\gamma_{CC} = 10.99$, $\gamma_{NN} = 13.03$ and $\gamma_{OO} = 15.86$ in units of eV. For the orbital exponents of core integrals and bonding parameters the original values[13] were used in this calculation.

TABLE I

Molecular geometries adopted in this work (bond length in units of A)

Azomethin group	*n*-Butyl group
C—C 1.50	C—C 1.54
C=N 1.24	C—H 1.09
N—C 1.46	∠HCH=∠CCH=109.47°
∠CNC=∠NCC=∠NCH=120°	Methoxy group
Benzene ring	C—OCH_3 1.36
C—C 1.39	O—CH_3 1.35
C—H 1.00	∠COC = 121°
∠CCC=∠CCH=120°	∠OCH = 109.47°

The CNDO/S + CI calculation of MBBA was performed by a FACOM M-160 electronic computer under the permission of the JSPS 135th committee on the scientific use of computers. For BA the electronic states were calculated by a FACOM 270-30 electronic computer.

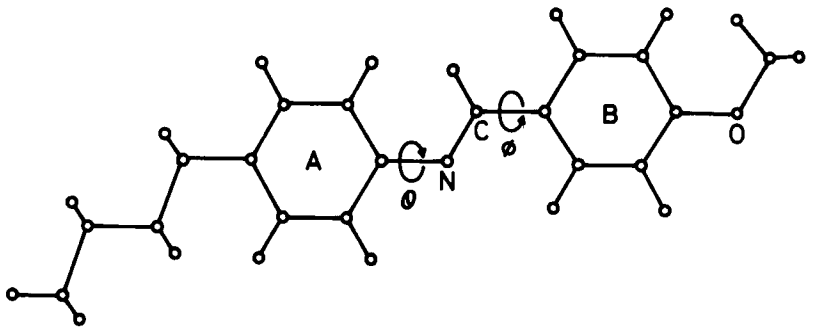

FIGURE 2 Molecular conformation and parameters of MBBA.

Effect of the twist of B ring of BA

At first the electronic spectra of BA are discussed here. The calculated oscillator strength and energy levels are shown in Figure 3 as a function of the twist angle ϕ of B ring out of the C=N—C plane.

As is shown in Figure 3, one strongly allowed transition appears in the long wavelength region of 250-300 nm. As the increase of the twist angle, the first $\pi\pi^*$ transition at 295 nm ($\phi = 0°$) becomes weaker and shifts to shorter wavelength-side (up to 260 nm at $\phi = 90°$). These features of the spectra are essentially the same as that caused by the steric hindrance to planarity of the conjugated system in linear alternant hydrocarbons. The steric hindrance exerts a hypochromic as well as a hypsochromic effect on the first intense $\pi\pi^*$ transition.[14] Of course, $n\pi^*$ transition appears weakly

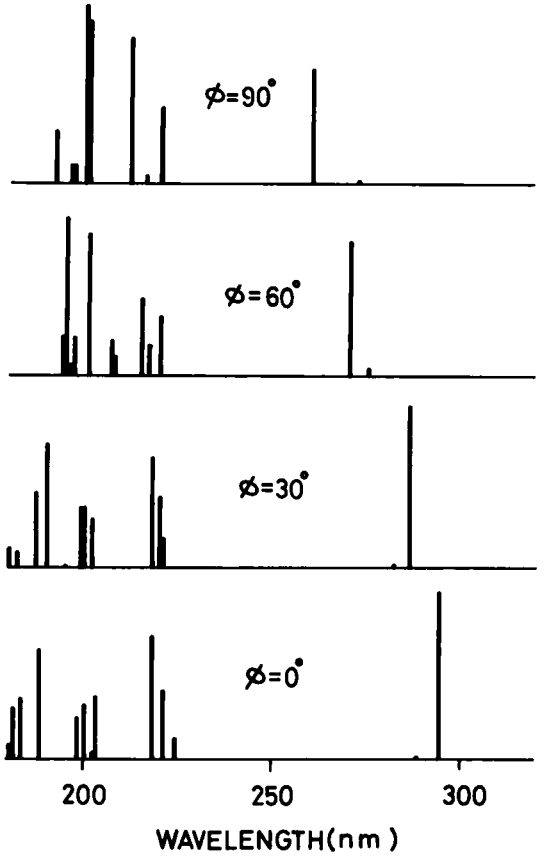

FIGURE 3 Calculated spectra of BA with several twist angles of B ring.

near the strong $\pi\pi^*$ transition, but these transitions do not interact to each other during this conformational change. These features of the calculated spectra are different from those of the observed spectra of BA and it may be said that the twist of B ring is not a main conformational change which is responsible to the spectral change of BA or MBBA. Hence the effect of another conformational change on the electronic spectra of BA is discussed as follows.

Effect of the twist of A ring of BA

The electronic transitions and oscillator strength of BA molecule were calculated as a function of the twist angle θ of A ring out of the C=N—C plane fixing the B ring in this plane. The result is shown in Figure 4.

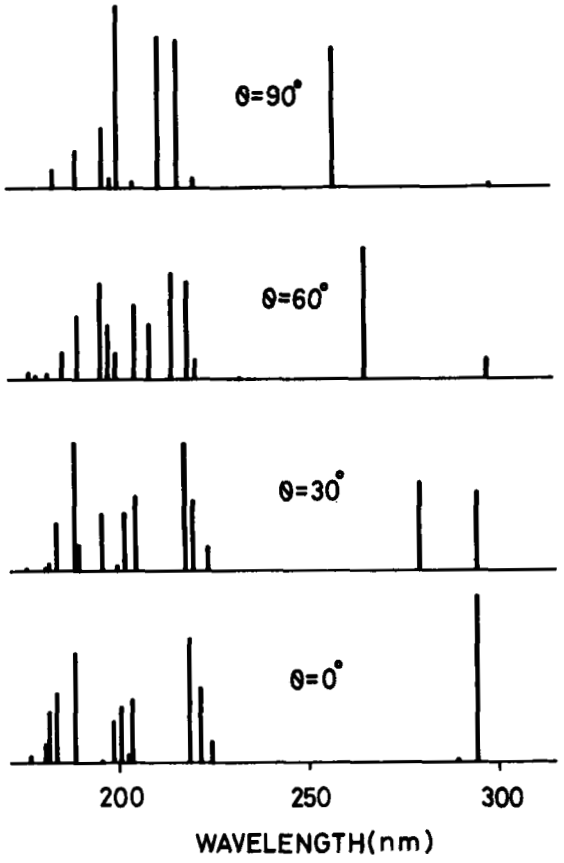

FIGURE 4 Calculated spectra of BA with several twist angles of A ring.

In the longer wavelength region (250–300 nm) of these spectra, two transitions show a remarkable behavior with the conformational change. For convenience the longer wavelength band is designated as band I and shorter one as band II, hereafter. The descriptions of the band I and II are summarized as follows:

a) *Planar conformation* ($\theta = 0°$) The band I is the first intense $\pi\pi^*$ transition from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecule orbital (LUMO) and has a transition moment along the long axis of the molecule. The band I has a character of an intramolecular charge transfer from the phenyl group to the benzylidenamine group as is revealed from the population analysis of the related molecular orbitals.

The band II is the $n\pi^*$ transition associated with the lone pair electrons on the N atom and was predicted to appear at 290 nm with weak intensity (oscillator strength = 0.017).

b) Twisted conformation Two kinds of interaction are important to understand the electronic structure of the twisted conformation of BA or MBBA. One of them is the $\pi\pi$ conjugation over the π electronic system and another one is the $n\pi$ conjugation between the lone pair electrons on N-atom and the π system on A ring. As the twist angle increases, the $\pi\pi$ conjugation decreases and the $n\pi$ conjugation increases.

In the twist conformation the $\pi\pi^*$ and $n\pi^*$ transitions interact strongly. Therefore, the bands I and II separate to each other and the band II borrows the intensity from the band I through the interaction and becomes a strongly allowed transition showing a remarkable blue shift. Both bands have a mixed character of $\pi\pi^*$ and $n\pi^*$ transitions and have nearly parallel transition moments to the long axis of the molecule.

c) Perpendicular conformation ($\theta = 90°$) Band I becomes a nearly forbidden $\pi\pi^*$ transition in this conformation. On the other hand, the band II becomes a very strong band situated at 245 nm and has a character of the local excited state on benzyliden amine group.

Five years ago, Skrabel *et al.*[15] reported the absorption spectra of various kinds of *p,p'*-substituted BA and 3H-indole, where the latter is a planar model compound of the former. As is revealed from their results, the shapes of UV spectra of many *p,p'*-substituted 3H-indoles are essentially the same as that of non-substituted 3H-indole which shows one strong band in the lower energy region. To the contrary, the *p,p'*-substituted BA's show a variety of relative positions and intensities of two bands in this region. This phenomenon may well be explained as follows. In a *p,p'*-substituted BA the A ring is twisted out of the C=N—C plane. The twist angle is dependent on the conjugation power of the substituents against the steric hindrance of the azomethin group. When the twist angle becomes larger, the separation between the two peaks becomes larger and the shorter wave-length peak becomes stronger. These results were found to be in good accordance with the present calculated results about the intensity variation and the shift of the two peaks in the twisted BA molecule. Hence these two peaks may well be assigned to the calculated bands I and II.

Effect of the twist of A ring of MBBA

The spectral change of MBBA associated with the twist of A ring was calculated as is shown in Figure 5.

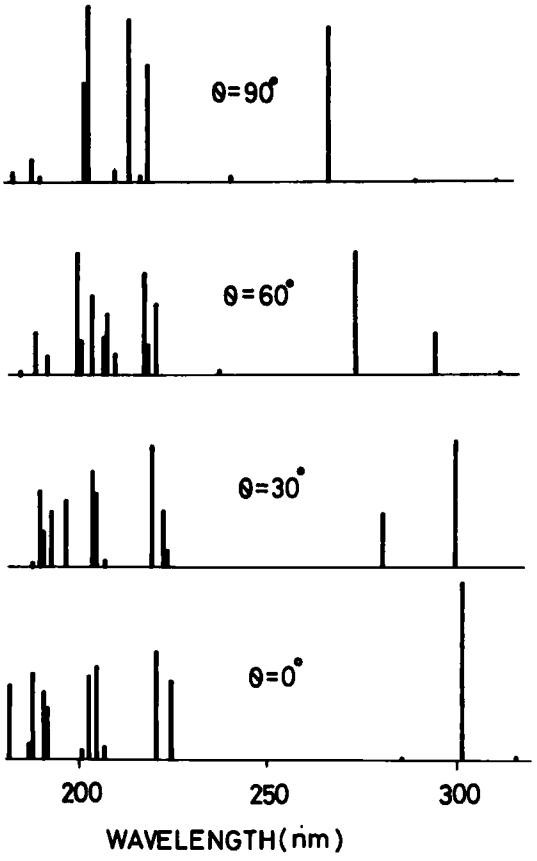

FIGURE 5 Calculated spectra of MBBA with several twist angles of A ring.

These results were interpreted similarly as in the above mentioned case because MBBA is also one of the *p,p'*-substituted BA. In the planar conformation the first intense $\pi\pi^*$ and weak $n\pi^*$ transitions were predicted to be at 302 nm and 286 nm, respectively. In the perpendicular conformation, the intense band appeared at 269 nm and weak one at 290 nm. These two bands offer a diagnostic information about the twist angle θ of MBBA through their relative positions and intensities. Of course, observed frequencies are often influenced by environmental factors such as solvent effect or crystal field and also the calculated transitions are not so reliable to draw straight forward any conclusion from the difference between the calculated results and observed ones. Calculated oscillator strengths are usually larger than observed ones. But, in this case, the ratio of oscillator strength of the bands I and II may well be adopted to the conformational analysis of BA or MBBA. The

calculated oscillator strength of MBBA is illustrated as a function of twist angle θ in Figure 6.

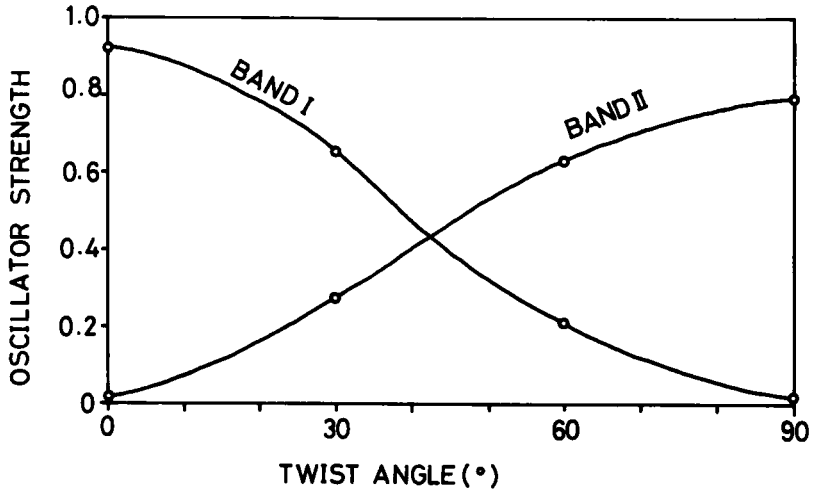

FIGURE 6 Calculated oscillator strength of band I and II of MBBA with several twist angles of A rings.

Total energies of BA and MBBA

Total energies of BA and MBBA were calculated for several twisted conformations by the CNDO/2 method.[16] The results are summarized in Table II.

TABLE II

Calculated total energy of BA and MBBA by the CNDO/2 method

θ	BA (eV)	MBBA (eV)
0°	−3047.0286	−4731.9830
30°	−3047.1423	−4732.1184
60°	−3047.2344	−4732.2795
90°	−3047.2575	−4732.3244
$\varepsilon(0°)-\varepsilon(90°)$	0.2289	0.3414
	(=5277 cal mol^{-1})	(=7871 cal mol^{-1})

PROPOSITION OF ROTATIONAL ISOMERISM OF MBBA

The difference between the calorimetric data for the stable and metastable solids of MBBA was pointed out in our previous paper.[1] And then the corresponding discrepancies were also observed in the Raman scattering[4,5]

at 1160–1170 cm^{-1} and below 250 cm^{-1} and in the UV absorption spectra.[6] In order to explain consistently these experimental and calculated results of MBBA, we took into account rotational isomers due to the twist of A ring out of the C=N—C plane. There is no evidence that B ring is coplanar with the C=N—C plane. Indeed, it was reported by X-ray analysis that the B ring is twisted out of the C=N—C plane by 10.3° in BA crystal.[12] The effect of the twist of B ring on the intensity of the first intense $\pi\pi^*$ band is relatively small compared with that of A ring as is seen from Figures 3 and 4. Furthermore, the patterns of intensity variation due to the twist of A ring are expected to be nearly isomorphic to each other for various twist angles of B ring. It may be a not so bad approximation to adopt the calculated θ variation curve of oscillator strength for the model conformation at $\phi = 0°$ in order to estimate the twist angle of A ring from the observed intensity ratio of bands I and II in the UV spectra of MBBA. Thus, estimated angles are summarized in Table III. The molecular conformation in vapor phase is conceived to be the same as that in the metastable solid which is the most unstable state among the established solids. The twist angle of 45.8° for the ethanol solution is relatively small compared with that for the cyclohexane solution. The cause for this result may be attributed to the enhancement of band I by the hydrogen-bond formation between MBBA and ethanol molecules.

TABLE III

Estimated angles of the twist of MBBA in various states

States	λ_{max} (nm)	f_{II}/f_I	θ
Isotropic liquid	323.0 282.5	1.74	52.5°
Nematic	324.7 283.2	1.70	52.0°
Metastable solid	330–340 272.6	4.23	66.3°
Stable solid	330–340 281.1	2.77	—
In ethanol	320.0 283.8	1.14	45.8°
In cyclohexane	321.5 279.2	2.03	54.8°
Vapour	310–315 256	4.27	66.5°

It was found about the conformation in the stable solid from Raman scattering[4] that two molecular conformations are mixed in the solid as explained later. Figure 7 shows the Raman spectra of MBBA in various

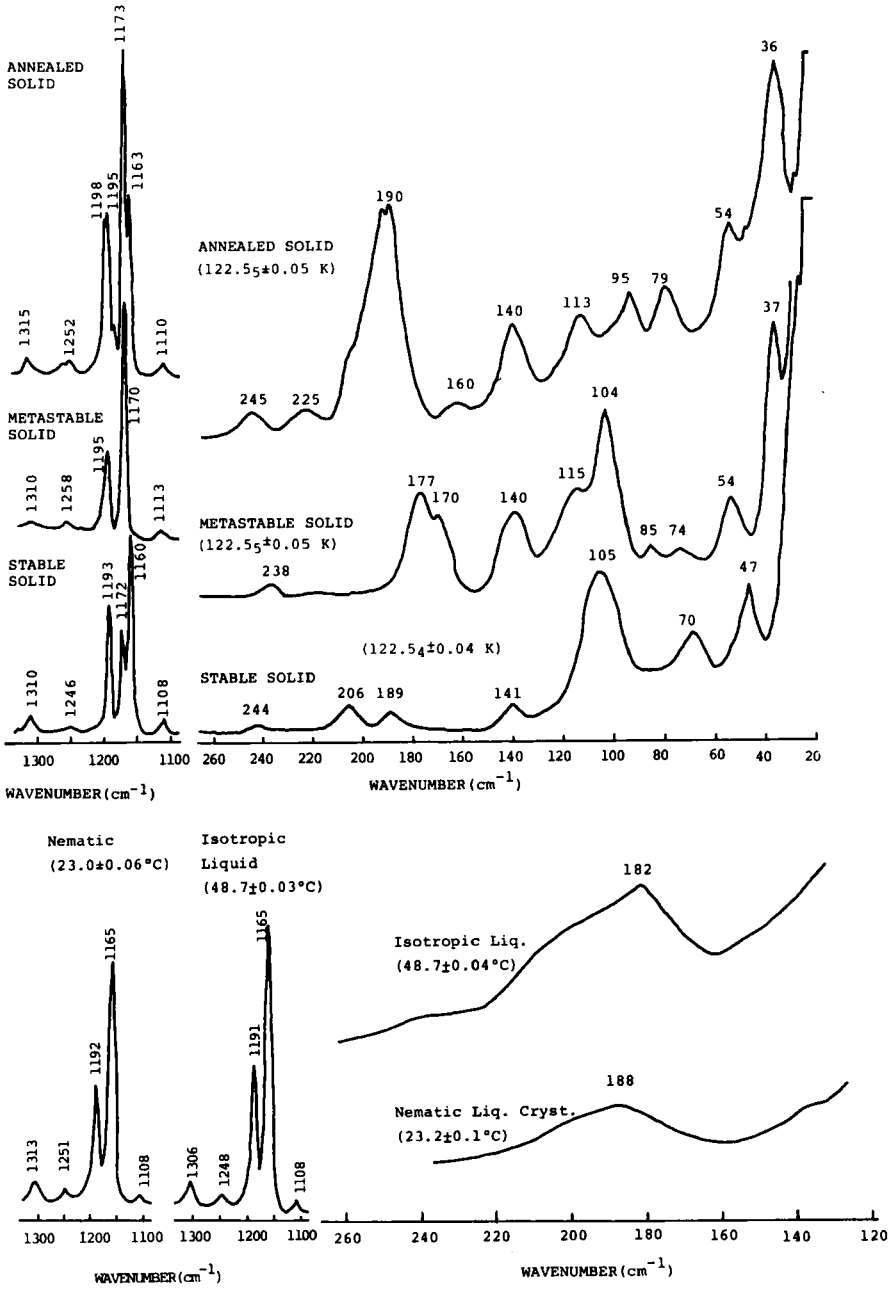

FIGURE 7 Low frequency Raman spectra below 250 cm^{-1} and Raman spectra in the region from 1100 to 1350 cm^{-1} of MBBA in various condensed states.

phases at 1160–1170 cm^{-1} and below 250 cm^{-1}, which are corresponding to the before mentioned variations in the UV spectra. The same results for the Raman spectra at 1160–1170 cm^{-1} were also observed by Brumant *et al.*[5] The annealed solid was established by annealing at about 0°C several times, and is in an intermediate state from the metastable to the stable.

The lowest frequency Raman band in the nematic and isotropic liquid states is a broad band centered at 188 and 182 cm^{-1}, respectively. Therefore, the bands below 140 cm^{-1} observed for different solids are very probable to be Raman lines of the lattice vibrations. The lowest intramolecular band was observed at 122.5 K as the doublet with two peaks at 177 and 170 cm^{-1} for the metastable solid, the band at 190 cm^{-1} with a shoulder at about 200 cm^{-1} for the annealed solid, and the two bands at 206 and 189 cm^{-1} for the stable solid, as is shown in Figure 7. These differences among the Raman spectra of various solid MBBA's are just corresponded to those in the strong Raman lines at 1160–1170 cm^{-1} shown in Figure 7. The line at 1160–1170 cm^{-1} may be assigned to the CCH deformation of benzene ring[17] the frequencies may be changed by the twist angles of A and B rings out of the C=N—C plane. Therefore, the bands at 200–170 cm^{-1} are very probable to be assigned to the internal rotation (twisting vibration) of A and B rings out of the C=N—C plane. This interpretation is consistent in the frequency-shifts accompanying with the stability of condensed states.

The band at 1160–1170 cm^{-1} for the annealed and stable solids splits into two peaks and their relative areas were estimated as 36% (1160 cm^{-1}) and 64% (1172 cm^{-1}) for the annealed solid and as 66% (1160 cm^{-1}) and 34% (1172 cm^{-1}) for the stable solid. This fact suggests that two molecular conformations with different twist angles are mixed in both solids with the ratio corresponding to the relative areas of the two peaks. We designate the rotational isomer with the frequency of 1160 cm^{-1} as S-I and that with the frequency of 1172 cm^{-1} as S-II. It was reported by Brumant *et al.*[5] that there is another state which has a molecular configuration different from that in the metastable solid. It has a strong Raman line at 1167 cm^{-1} at 80 K, this frequency being very near to the frequency observed in nematic and isotropic liquid states. So, it was assumed that in this state of solid MBBA the molecule has the same conformation as those in the nematic state, which is denoted as N-form. The molecular conformation in metastable solid MBBA was denoted as M-form. The data about the Raman CCH deformation bands of MBBA at 122.5 K and 80 K are summarized in Table IV.

The distance (r) between the H-atom (attached to double bond carbon) and a H-atom (attached to A ring) is changed by internal rotation. The interatomic interaction between non-bonded hydrogen atoms was studied by Boer,[18] Buckingam[19] and Shimanouchi[20] and analytical expressions of potential functions were presented.[18,19] Using the exponential type of

TABLE IV

Observed Raman scattering frequency of CCH deformation of MBBA

States	ν (cm^{-1})	Temperature (K)
Isotropic liquid	1165	321.85 ± 0.03
Nematic	1165	296.15 ± 0.06
Metastable solid	1170	122.5_7 ± 0.07
Stable solid	1160	122.5_2 ± 0.02
	1172	
Annealed solid	1160	122.5_5 ± 0.01
	1172	
N-form (Form II in Ref. 4)	1167	80

potential function presented by Boer and assuming a harmonic oscillation for the CCH deformation vibration, we derived the next relation between the frequency (ν) of the CCH deformation of C_6H_4 ring and H ... H distance(r) as follows:

$$\nu^2 = \nu_0^2 - B[\exp(-Cr)], \tag{1}$$

where ν_0, B and C are constants. r may be given as a function of the twist angle θ in the following:

$$r_1^2 = r_0^2 + \left[4.14\left\{\sin\left(\frac{\theta}{2}\right)\right\}\right]^2 \quad \text{or} \quad r_2^2 = r_0^2 + \left[4.14\left\{\cos\left(\frac{\theta}{2}\right)\right\}\right]^2, \tag{2}$$

where r_0 is r_1 at $\theta = 0°$. We assumed as $\nu_0 = 1177\ cm^{-1}$ (the frequency of the CCH deformation of benzene), $r_0 = 1.780$ A and $r = (r_1 + r_2)/2$, and determined two constants (B = 1.5973×10^6 and C = 1.5893) from the observed frequencies (1165 and 1170 cm^{-1}) and the estimated twist angles (52.0° and 66.3°) for N and M forms, respectively. Then, we evaluated the twist angles for S-I and S-II forms from the observed Raman frequencies using Eq. (1). The result gives that $\theta_{S\text{-}I} = 44.4°$ and $\theta_{S\text{-}II} = 82.7°$. At this stage, we had the least data necessary to determine the two twist angles and could not estimate the error limits originated from the applied model and observed data. Hence the twist angles determined here should be examined by other methods. If the Boltzmann distribution is established between the *S*-I and *S*-II forms in the stable solid at 122.52 K, at which Raman spectrum of the stable solid was measured, we find from the ratio of number of molecules that the energy difference, $V_{S\text{-}II}$–$V_{S\text{-}I}$, between them is about 160 cal mol^{-1}. Also, using these values of $\theta_{S\text{-}I}$ and $\theta_{S\text{-}II}$, it may be concluded from the observed value of f_{II}/f_I, 2.77, for the stable solid at 19_3°C that 45.2% of molecules are in *S*-I conformation and 54.8% are in *S*-II one. This may be due to that

sample of which the UV spectrum in the stable solid (shown in Figure 1 of Ref. 6) was observed did not transform completely from the metastable to the stable state and was in an intermediate state.

If the potential energy for the internal rotation of A and B rings is given by

$$V = \frac{1}{2}\left[V_0 + \sum_n V_n\{1 - \cos(n\theta)\}\right], \tag{3}$$

the equation, $[(\delta V)/(\delta\theta)] = (\frac{1}{2})\sum_n nV_n[\sin(n\theta)]$, must be equal to zero at $\theta = \theta_{S\text{-I}}, \theta_N, \theta_M, \theta_{S\text{-II}}$. Assuming the twist motion as harmonic vibration we can obtain the relation:

$$\left[\frac{(\delta^2 V)}{(\delta\theta^2)}\right] = \left(\frac{1}{2}\right)\sum_n n^2 V_n[\cos(n\theta)] \simeq 4\pi^2 c^2 \nu^2 I, \tag{4}$$

where c is the light velocity, ν is the twisting frequency and I is the reduced moment of inertia of the internal rotation. Using the values of the twisting frequency for *S*-I, N, M and *S*-II forms ($\nu_{S\text{-I}} = 206$, $\nu_N = 188$, $\nu_M = 177$ and $\nu_{S\text{-II}} = 190$ cm^{-1}) and the calculated value of $I = 13.3438 \times 10^{-39}$ g cm^2, we can obtain four relations. It is reasonable for MBBA that n is even in consideration of the molecular structure.

Taking into account the energy difference between a planar and perpendicular conformations calculated by means of the standard CNDO/2 method and the obtained value for $V_{S\text{-II}} - V_{S\text{-I}}$, we propose a potential energy curve for the solid MBBA which can give a reasonable interpretation for the experimental data and the calculated results. The potential function is obtained as follows:

$$\begin{aligned} V = (\tfrac{1}{2})[&(17.6372) + (-6.3934)(1 - \cos 2\theta) + (-3.3851)(1 - \cos 4\theta) \\ &+ (-1.1231)(1 - \cos 6\theta) + (0.79467)(1 - \cos 8\theta) \\ &+ (-1.1267)(1 - \cos 12\theta) + (-0.74326)(1 - \cos 14\theta) \\ &+ (-0.06436)(1 - \cos 20\theta) + (-0.51910)(1 - \cos 24\theta) \\ &+ (0.16332)(1 - \cos 28\theta) + (-0.23629)(1 - \cos 36\theta) \\ &+ (-0.04702)(1 - \cos 38\theta) + (0.15742)(1 - \cos 40\theta) \\ &+ (0.06698)(1 - \cos 48\theta)], \end{aligned} \tag{5}$$

where $V_{S\text{-I}}$ is zero and V is given in units of Kcal mol^{-1}. This potential energy curve is shown in Figure 8.

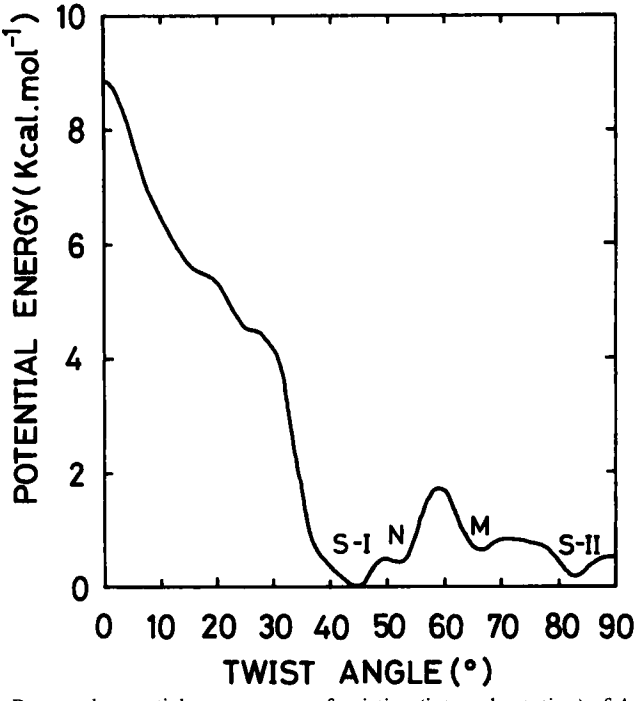

FIGURE 8 Proposed potential energy curve of twisting (internal rotation) of A and B rings for MBBA.

DISCUSSION

We attempted to calculate the energy difference among the rotational isomers owing to butyl end group of MBBA proposed by Castro and Elbaum[21] using the CNDO/2 method. The result gives that the energy difference between TT and TG is about 3.51 Kcal mol^{-1} and that between TT and GT is 8.20 Kcal mol^{-1}. This suggests that it is unreasonable to interpret the difference between the entropy of the stable and metastable solids as being due to the motion of the *n*-butyl group considering the order of magnitude of enthalpies of transition from solids to nematic states.[1,2]

Although the obtained potential function (Eq. 5) is not satisfactory since the available informations about the twisting are not enough, we can conclude that the potential energy curve for the internal rotation of A and B rings in condensed states is a modified one slightly from that of a free MBBA molecule calculated by the CNDO/2 method. In other words, the small modification is originated from intermolecular interactions among MBBA molecules and plays an important role in the phenomenon of polymorphism of solid MBBA.

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