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Electronic Structures and Conformations of *N*-Benzylideneanilines. II. Photoelectron Spectral Study

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Electronic structures and molecular conformations have been studied for *N*-benzylideneaniline and its 2-methyl, 2,6-dimethyl, and their 4-nitro derivatives by photoelectron spectroscopy. The lower energy bands are analyzed in detail, and the twist angles θ_N of the anilino benzene rings (ring A) about the carbon-nitrogen bonds are estimated by examining the effect caused by a methyl substitution. It is concluded that *N*-benzylidene-4-nitroaniline takes a more twisted conformation than *N*-benzylideneaniline.

In a preceding paper,[1)] the electronic structures and the molecular conformations of *N*-benzylideneaniline and its derivatives bearing 2-methyl, 2,6-dimethyl, and/or 4-nitro groups on the aromatic nuclei on the nitrogen atoms (ring A) (compounds **1**—**6**) have been investigated by electronic absorption spectroscopy.

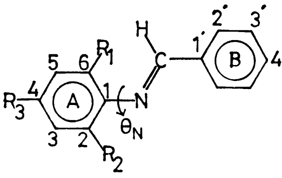
Concerning the photoelectron spectra (PES)[2)] of *N*-benzylideneanilines, four reports have been published, but there has been some controversy on the PES band assignment and the molecular conformations estimated by this method.[3—6)]

As regards to the twist angle θ_N (see the formula shown below) of *N*-benzylideneanilines, Bally *et al.* have recently estimated the twist angle θ_N to be approximately 36° by PES.[5)] Gas phase electron diffraction study has determined the twist angle θ_N to be about 52°.[7)] The calculations by the PCILO method with geometry optimization,[8)] and by the NDDO method[9)] have indicated that *N*-benzylideneaniline is twisted in θ_N by 36° and 65°, respectively. Concerning the PES of substituted *N*-benzylideneanilines, Klasinc *et al.* have investigated *N*-benzylideneaniline and some of its derivatives bearing methoxyl and/or nitro groups *etc.* as ring substituents and tried the HMO calculations.[6)] They explained the results on the ground that these compounds take twisted conformations but on the assumption that the twist angle θ_N would be the same among the compounds examined. However, this assumption seems not to be adequate as has been described in the preceding paper.[1)]

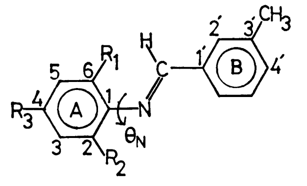
In order to get deeper insight into these problems, PES of *N*-benzylideneanilines **1**—**6** have been investigated. An attempt has been made to assign the PES bands precisely, and to estimate the molecular conformations of these compounds. The present results support our conclusion in the preceding paper that *N*-benzylidene-4-nitroaniline **4** is more twisted than *N*-benzylideneaniline **1**.

Results and Discussion

Photoelectron spectra have been measured for **1**—**6** and their 3′-methyl derivatives **7**—**12**; the latters are employed to assist the band assignments of the formers. Figures 1 and 2 show the PES of **1**—**6**. Table 1 summarizes the vertical ionization energies, E_{iv}, of **1**—**12** together with those of some related compounds for the sake of comparison.



1: $R_1=R_2=R_3=H$
2: $R_1=H$, $R_2=CH_3$, $R_3=H$
3: $R_1=R_2=CH_3$, $R_3=H$
4: $R_1=R_2=H$, $R_3=NO_2$
5: $R_1=H$, $R_2=CH_3$, $R_3=NO_2$
6: $R_1=R_2=CH_3$, $R_3=NO_2$



7: $R_1=R_2=R_3=H$
8: $R_1=H$, $R_2=CH_3$, $R_3=H$
9: $R_1=R_2=CH_3$, $R_3=H$
10: $R_1=R_2=H$, $R_3=NO_2$
11: $R_1=H$, $R_2=CH_3$, $R_3=NO_2$
12: $R_1=R_2=CH_3$, $R_3=NO_2$

In the present work, in order to assign the PES bands precisely and to estimate the twist angles, θ_N, the effect of methyl substitution on the ionization energy has been extensively employed, which has been successfully applied to analyze the PES of styrenes,[10)] for example.

Band Assignments. As shown in Fig. 1 and Table 1, *N*-benzylideneaniline **1** shows three groups of bands in the range of 8—10.5 eV. In this region, *trans*-stilbene has five π-bands.[11)]

The first band of **1** has previously been assigned to the π-orbital corresponding to the highest occupied π-orbital of *trans*-stilbene delocalized over the entire molecular framework.[4)] The first bands of the other *N*-benzylideneanilines studied can be reasonably correlated with the first band of **1**.

Compounds **1**, **2**, and **3** exhibit bands at nearly the same ionization energies, E_{iv}, 9.47 (shoulder), 9.49 (shoulder), and 9.47 eV, respectively, irrespective of 2-methyl, and 2,6-dimethyl substitution on the ring A. This fact suggests that these bands do not correspond to the π-orbital localized on the ring A. On the other hand, on 3′-methyl substitution on the benzylidene benzene ring (ring B), these bands are sensitively shifted to the low energy side by 0.34, 0.36, and 0.48 eV, respectively, as shown in Table 1. Accordingly, it is reasonable to correlate these bands with the 9.38 eV π-orbital band of *N*-benzylidenemethylamine.[5)] Likewise, the 9.51 eV band of **4** and one of the 9.50 eV

Table 1. Vertical ionization energies, E_{iv}, of *N*-benzylideneanilines **1**—**12** and related compounds

Compound	E_{iv}/eV					
	Band 1	2	3	4	5	6
N-Benzylideneaniline **1**	8.25	9.17	9.47^{sh}	9.97	11.3	
N-Benzylidene-2-methylaniline **2**	8.06	8.80^{sh}	9.04	9.49^{sh}	9.88	11.0^{3}
N-Benzylidene-2,6-dimethylaniline **3**	8.00	8.54	8.94	9.47	9.86	10.9^{6}
N-Benzylidene-4-nitroaniline **4**	8.76	9.51	9.73	10.48	10.71	11.6^{3}
N-Benzylidene-2-methyl-4-nitroaniline **5**	8.66	9.50	9.78^{sh}	10.61	11.6^{0}	
N-Benzylidene-2,6-dimethyl-4-nitroaniline **6**	8.51	9.23	9.74	10.50	11.2^{8}	
N-(3-Methylbenzylidene)aniline **7**	8.07	8.92^{sh}	9.13	9.90	11.1^{5}	
N-(3-Methylbenzylidene)-2-methylaniline **8**	8.00	8.74	9.13^{sh}	9.78	10.94	
N-(3-Methylbenzylidene)-2,6-dimethylaniline **9**	7.90	8.47^{sh}	8.73	8.99	9.80	10.73
N-(3-Methylbenzylidene)-4-nitroaniline **10**	8.58	9.14	9.72	10.67		
N-(3-Methylbenzylidene)-2-methyl-4-nitroaniline **11**	(8.49)[a)]	(9.14^{sh})	(10.43)	(11.6)		
N-(3-Methylbenzylidene)-2,6-dimethyl-4-nitroaniline **12**	8.43	8.98^{sh}	9.44^{sh}	10.21	10.55	11.2^{0}
trans-Stilbene[b)]	7.87	9.08	9.50	10.51	11.3	
trans-Azobenzene[c)]	8.46	8.77	9.30	9.77	11.6	
Benzene[d)]	9.23	11.67	12.32	13.97		
Nitrobenzene[d)]	9.88	10.29	10.97	11.15	12.56	
m-Xylene[d)]	8.71	9.03	11.24			
N-Benzylidenemethylamine[e)]	8.77	9.38	10.87	11.71		

a) No well-resolved spectrum was observed. b) Ref. 11. c) Ref. 4. d) Ref. 13. e) Ref. 5.

bands of **5** can be correlated with the same type of π-orbital since these bands are not sensitive to 2-methyl substitution on the ring A but sensitive to 3′-methyl substitution on the ring B (ΔE_{iv}=0.37 and 0.36 eV in going from **4** to **10** and **5** to **11**, respectively).

In the nitro derivative **4**, one can expect that π-orbitals mainly localized on the ring B should be lower in ionization energy than those on the ring A since the nitro group should increase the ionization energies of orbitals mainly localized on the ring A. This consideration suggests that one of the doubly degenerate 9.73 eV bands of **4** is correlated with the first π-band of nitrobenzene at 9.93 eV.[12,13)]

The second band of **3** at 8.54 eV is insensitive to 3′-methyl substitution on the ring B (ΔE_{iv}=0.07 eV in going from **3** to **9**), and is closely located to the 8.71 eV $a_2\pi$ band of *m*-xylene.[12,13)] So, it may be reasonably assigned to the π-orbital corresponding to the first $a_2\pi$ band of *m*-xylene. The ionization energy of the first $a_2\pi$ band of *m*-xylene is smaller than that of the $e_{1g}\pi$ band of benzene by 0.52 eV due to the destabilization of the $a_2\pi$ type orbital of the benzene ring by meta-dimethylation. Therefore, the bands corresponding to the 8.54 eV band of **3** are expected to appear around 9.06 eV for **1** and 8.80 eV for **2**. Thus, one of the degenerate 9.17 eV bands of **1** and the 8.80 eV band of **2** may safely be correlated with the 8.54 eV band of **3**. This assignment is supported by the fact that the 8.80 eV band of **2** is not sensitive to 3′-methyl substitution (ΔE_{iv}=0.06 eV in going from

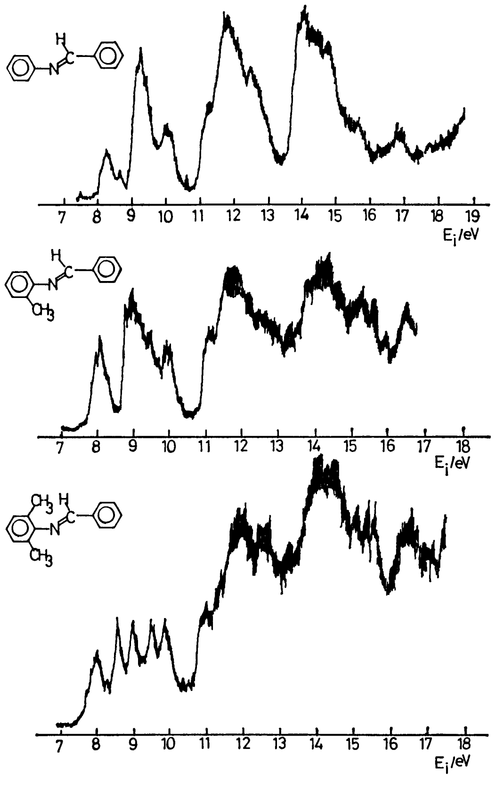


Fig. 1. Photoelectron spectra of **1**—**3**.

2 to **8**). Similarly, one of the degenerate 9.50 eV bands of **5** and the 9.23 eV band of **6** can be correlated with the 9.73 eV band of **4** corresponding to the first π-band of nitrobenzene.

Assignment of the N-lone pair orbital is now considered by inspecting the well-resolved PES of **3**. As mentioned before, its 8.54 and 9.47 eV bands correspond to the π-orbitals mainly localized on the ring A and the ring B, respectively. The CNDO/S[14] calculations suggest that its 8.94 eV band corresponds to the 8.77 eV π-band of *N*-benzylidenemethylamine and the 9.86 eV band corresponds to the N-lone pair orbital, and, in fact, the 9.86 eV band is not so sensitive to 3′-methyl substitution (ΔE_{1v}=0.06 eV in going from **3** to **9**) as the 8.94 eV band (ΔE_{1v}=0.21 eV in going from **3** to **9**). However, as shown in the preceding paper,[1] *N*-benzylideneanilines examined take, more or less, twisted conformations so that the N-lone pair orbital will interact with π-orbitals to some extent. Therefore, it is not adequate to assign a specific band to the pure N-lone pair orbital, and the 9.86 eV band of **3** has to be considered as "delocalized" N-lone pair orbital. This interpretation seems in keeping with recent postulation by Klasinc *et al.*[6]

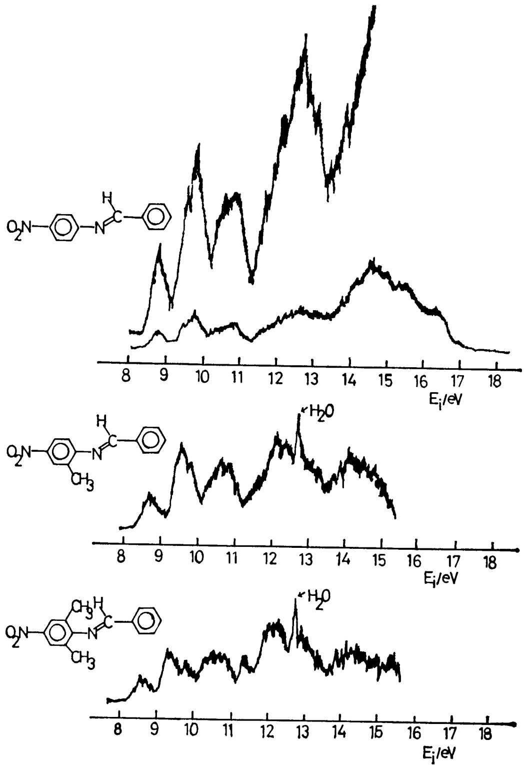


Fig. 2. Photoelectron spectra of **4**—**6**.

The above considerations have enabled us to draw the band correlation diagram as shown in Fig. 3.

Estimation of the Twist Angles, θ_N. We now wish to report an approach to estimate the twist angles θ_N in *N*-benzylideneanilines and present the evidence that the twist angle θ_N is significantly changed by the introduction of 4-nitro group on the ring A.

In the present method, one considers the first band energy difference ΔE_{1v} between **1** and **2** and that between the corresponding 4-nitro derivatives **4** and **5** as the perturbation caused by the substitution of a methyl group for 2-hydrogen on the ring A. Then, the ΔE_{1v} is calculated with changing the twist angle θ_N to find out a value which coincides with the observed ΔE_{1v} value. In the calcualtions, the ΔE_{1v} is estimated by the following equation derived on the basis of the first order perturbation treatment,[15]

$$\Delta E_{1v} = 0.0528 + 1.0110 a_J$$
$$a_J = \sum_{\xi} (3C_{J\xi}^2 + C_{J\tau}^2 + C_{J\tau'}^2)/3,$$

where ξ denotes the position of the methyl substitution and τ and τ′ denote the ortho-positions to that

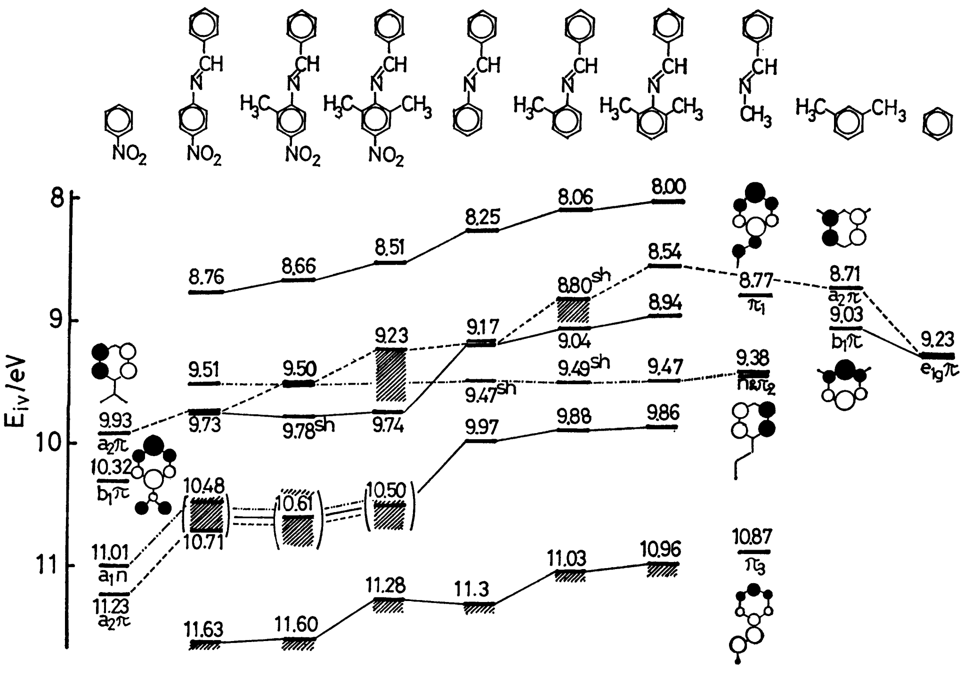


Fig. 3. The observed band correlation diagram for **1**—**6**.

of the methyl substitution. C_{JK} is the coefficient of the K-th AO in the J-th MO. C_{JK}'s were calculated for **1** and **4** by the CNDO/S[14] method at various twist angles θ_N. Then, the corresponding ΔE_{iv} values were calculated by the above equation and plotted in Fig. 4 against θ_N.

As is evident in Fig. 4, the calculated ΔE_{iv}'s become closer to the observed one in the range of smaller twist angle θ_N for **1** and of larger twist angle θ_N for **4**. Estimation of the twist angle θ_N by using the van der Waals radius of a hydrogen atom indicates that the twist angle θ_N for **1** is larger than 48°. Therefore, on taking into account of the probable error (0.026 eV **) accompanying the PES measurements and the calculations of ΔE_{iv}, the twist angle θ_N for **1** is estimated to be $48° \lesssim \theta_N \lesssim 55°$. The present result accords with that recently determined by the gas phase electron diffraction (ED) method, 52°.[7]

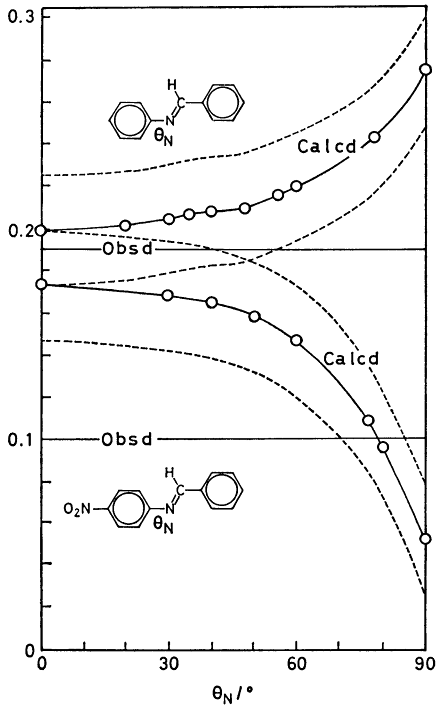


Fig. 4. Variations of the calculated ΔE_{iv} as a function of θ_N.
The broken lines indicate probable error.

Similarly, the twist angle θ_N for **4** can be estimated to be $70° \lesssim \theta_N \lesssim 85°$. These results, to our knowledge, for the first time by PES, indicate that **4** takes a more twisted conformation than **1**. The significant increase in the twist angle θ_N caused by the introduction of 4-nitro group on the ring A can be rationalized in terms of enhancement of conjugation between the N-lone pair and the aromatic π-system due to the strong electron-withdrawing property of the nitro group.

In the case of **1**, the present result on the twist angle θ_N is in qualitative agreement with that given by Bally *et al.*[5] Concerning the first band of **1**, 2-methyl substitution on the ring A shifts the band to lower energy side by 0.19 eV; however, additional 6-methyl substitution (from **2** to **3**) further causes the shift to lower energy side but by only 0.06 eV. Thus, in the series of **1**—**3**, the methyl substituent effect is not additive. The band shape of **1** in the range of 7.8—10.5 eV is very similar to that of **2**. However, it is drastically changed by the introduction of 2,6-dimethyl groups (see Fig. 1). These facts suggest that the twist angle θ_N is significantly increased by the introduction of the two methyl groups because of their steric effect. The twist angle θ_N for **3** can thus be estimated to be ≳77° by taking into account of the van der Waals repulsion between the imidoyl hydrogen atom and the 2-methyl group of the ring A.

On the other hand, the introduction of 4-nitro group on the ring A increases the ionization energy by 0.51 eV and the successive methyl substitutions (in going from **4** to **5**, and to **6**) decrease the ionization energy by 0.10 and 0.15 eV in each step. In this case, the methyl substituent effect appears to be roughly additive. This fact suggests that the twist angle θ_N is not changed drastically even by the 2,6-dimethyl substitution of **4**. These results are consistent with our results by electronic absorption spectroscopy.[1]

TABLE 2. COMPARISON OF THE TWIST ANGLE, θ_N

Compound	Method (state)					
	PES (gas)	ED (gas)	UV[a] (solution)	XD (solid)	MO	v.d.W.[b]
N-Bezylideneaniline **1**	(48)[b] –55° 36°[c]	52°[d]	30—35°	55.2°[e]	36°[f] 65°[g]	≳48°
N-Benzylidene-2-methylaniline **2**	(48)[b] –55°		40—45°			≳48°
N-Benzylidene-2,6-dimethyl-aniline **3**	≳(77°)[b]		70—80°			≳77°
N-Benzylidene-4-nitroaniline **4**	70—85°		not far from 90°	50.2°[e,h]		≳48°
N-Benzylidene-2-methyl-4-nitroaniline **5**	70—85°					≳48°
N-Benzylidene-2,6-dimethyl-4-nitroaniline **6**	≳(77°)[b]					≳77°

a) Ref. 1. b) Estimated using the van der Waals radii for a methyl group and a hydrogen atom. c) Ref. 5. d) Ref. 7. e) Ref. 16. f) The PCILO method, Ref. 8. g) The NDDO method, Ref. 9. h) Value observed for *N*-(4-methylbenzylidene)-4-nitroaniline.

** The probable error was calculated by using the data in Table 3 of Ref. 15.

In Table 2 are summarized the twist angles θ_N for **1**—**6** estimated by various methods. It seems to be of interest, that at least in solutions and in the gas phase, the electronic effect of a nitro group as well as the steric effect by bulky 2,6-dimethyl groups may result in considerable twisting of the ring A from the azomethine skeletal plane. It is worth pointing out that in this class of compounds their molecular conformations may be sensitively changed by the electronic effect of a substituent introduced in the aromatic ring on the nitrogen atom.

Experimental

Materials. *N*-benzylideneanilines **1**—**6** were prepared as described in the preceding paper,[1] and other *N*-benzylideneanilines employed were similarly prepared. The new compounds **8**, bp 142—143 °C/7 mmHg, **9**, bp 152—153 °C/2 mmHg, **10**, mp 72—73 °C, **11**, mp 101—102 °C, and **12**, mp 104—105.5 °C, gave the satisfactory results of elemental analyses.

Spectral Measurements. Photoelectron spectra were recorded on the instrument reported previously using the He I resonance line (21.22 eV) as the excitation source, and were calibrated using Xe as an internal standard.[10] The sample inlet and target chamber system was heated up to *ca.* 110—140 °C to obtain sufficient vapor pressure.

Theoretical Calculations

The CNDO/S calculations were carried out with a FACOM 230-75 computer at the Institute of Physical and Chemical Research. The geometrical structures were properly assumed on the basis of appropriate data given in Ref. 16 just as in Ref. 1.

References

1) R. Akaba, K. Tokumaru, and T. Kobayashi, *Bull. Chem. Soc. Jpn.*, **53**, 1993 (1980).

2) D. W. Turner, C. Baker, A. D. Baker, and C. R. Brundle, "Molecular Photoelectron Spectroscopy," John Wiley, London (1970).

3) H. Goetz, F. Marschner, and H. Juds, *Tetrahedron*, **30**, 1133 (1974).

4) T. Kobayashi, K. Yokota, and S. Nagakura, *J. Electron Spectrosc. Relat. Phenom.*, **6**, 167 (1975).

5) T. Bally, E. Haselbach, S. Lanyiova, F. Marschner, and M. Rossi, *Helv. Chim. Acta*, **59**, 486 (1976).

6) L. Klasinc, B. Rušćić, G. Heinrich, and H. Güsten, *Z. Naturforsch., Teil B*, **32**, 1291 (1978).

7) M. Traetteberg, I. Hilmo, R. J. Abraham, and S. Ljunggren, *J. Mol. Struct.*, **48**, 395 (1978).

8) P. Jacque and J. Faure, *Theor. Chim. Acta*, **46**, 307 (1977).

9) H. J. Hofmann and F. Birnstock, *J. Mol. Struct.*, **44**, 231 (1978).

10) T. Kobayashi, K. Yokota, and S. Nagakura, *J. Electron Spectrosc. Relat. Phenom.*, **2**, 449 (1973).

11) T. Kobayashi, K. Yokota, and S. Nagakura, *Bull. Chem. Soc. Jpn.*, **48**, 412 (1975).

12) T. Kobayashi and S. Nagakura, *Chem. Lett.*, **1972**, 903.

13) T. Kobayashi and S. Nagakura, *Bull. Chem. Soc. Jpn.*, **47**, 2563 (1974).

14) R. L. Ellis, G. Kuehnlentz, and H. H. Jaffé, *Theor. Chim. Acta*, **26**, 131 (1972).

15) E. Heilbronner, V. Hornung, F. H. Pinkerton, and S. F. Thames, *Helv. Chim. Acta*, **55**, 289 (1972).

16) H. B. Bürgi and J. D. Dunitz, *Helv. Chim. Acta*, **53**, 1747 (1970).