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# Most Stable Conformer of 2-Phenylpropanal Elucidated by Supersonic Jet Spectroscopy

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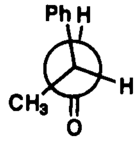
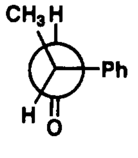
**Abstract:** The most stable conformer of 2-phenylpropanal is elucidated by supersonic jet spectroscopy. Only a single conformer of 2-phenylpropanal exists under jet conditions. This conformer shows two bands with red shifts of 32 and 65 cm$^{-1}$ when it is complexed with argon. The former corresponds to the mono-Ar complex and the latter to the di-Ar complex. From these results, it is concluded that the most stable conformer is **1**, in which the CO group bisects the included angle defined by the C−CH$_3$ and C−H bonds.

The origin of asymmetric induction has attracted much interest from both theoretical and practical points of view. In order to better understand and to predict the stereoselectivity of the nucleophilic addition reaction to chiral aldehydes and ketones, empirical models for the transition state structure of the addition reaction have been proposed: Cram,[1] Karabatsos,[2] and Felkin−Anh[3] models. It is also important to know the ground state conformation of chiral aldehydes and ketones in order to rationalize the preference for attack on the diastereotopic faces of the carbonyl compounds. The extent of 1,2-asymmetric induction has been judged frequently by the diastereoisomer ratio of the products obtained from the addition to 2-phenylpropanal.[4] However, to the best of our knowledge, little is known on the ground state conformations of acyclic chiral aldehydes including 2-phenylpropanal. The evidence obtained here, by using supersonic jet spectroscopy,[5] strongly supports that the most stable conformer of 2-phenylpropanal is **1** in which the CO group bisects the included angle defined by the C−CH$_3$ and C−H bonds.



**1**



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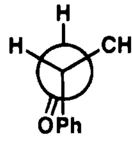

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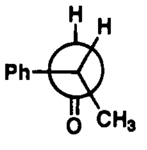

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## Results and Discussion

The absorption spectrum of 2-phenylpropanal was measured in cyclohexane solution (Figure 1, top). Figure 1, bottom, shows the laser-induced fluorescence excitation spectrum of jet-cooled 2-phenylpropanal around the 280−290 nm region. Band A at 34 757 cm$^{-1}$ was assigned to the band origin. The other bands appearing in Figure 1 were assigned by measuring the dispersed fluorescence (DF) spectra, as shown in Figure 2. As can be seen in Figure 2, the DF spectra of the bands in the first 750 cm$^{-1}$ region above the band origin have a structure in which the $X^1_1$ band intensity is very strong, where X is the vibrational mode. Therefore, these bands are assigned to the vibronic bands belonging to band A. The DF spectra of the bands whose energies are more than 950 cm$^{-1}$ above the band origin (A) became very weak and showed a very broad structure, which may be due to intramolecular vibrational redistribution (IVR). Therefore, most of the intense peaks above the band origin A are assigned to the vibronic bands of A. Accordingly, it is clear that only a single conformer exists under the present jet conditions.

It is not established unambiguously that the relative population of the conformers of 2-phenylpropanal under jet conditions is equal to that at room temperature. However, in general, the interconversion between conformers during the supersonic expansion is thought to be small. For example, Hopkins et al.[6a] showed that two conformers (trans and gauche) of *n*-alkylbenzene ($n \geq 3$) are populated with comparable ratios in the supersonic jet, and Ito et al.[5h] also demonstrated that the relative population of cis- and trans-isomers of *m*-substituted phenol in a supersonic jet is not so different from that at room temperature. From these results, the interconversion among the conformers during the adiabatic expansion seems to be small and the relative population of the conformers in the supersonic jets may be not so different from that at room temperature. Therefore, it may be concluded that 2-phenylpropanal adopts a single conformation even at room temperature in the gas phase.

To clarify the stable conformation of 2-phenylpropanal, we measured the electronic spectra of the van der Waals complexes with Ar. The idea comes from the measurement by Hopkins

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(1) Cram, D. J.; Abd Elhafez, F. A. *J. Am. Chem. Soc.* **1952**, *74*, 5828.

(2) Karabatsos, G. J. *J. Am. Chem. Soc.* **1967**, *89*, 1367.

(3) Anh, N. T.; Eisenstein, O. *Nouv. J. Chim.* **1977**, *1*, 61. Anh, N. T. *Top. Curr. Chem.* **1980**, *88*, 145.

(4) Yamamoto, Y.; Maruyama, K. *J. Am. Chem. Soc.* **1985**, *107*, 6411.

(5) (a) Seeman, J. I.; Secor, H. V.; Breen, P. J.; Grassian, V. H.; Bernstein, E. R. *J. Am. Chem. Soc.* **1989**, *111*, 3140. (b) Yamamoto, S.; Okuyama, K.; Mikami, N.; Ito, M. *Chem. Phys. Lett.* **1986**, *125*, 1. (c) Seeman, J. I.; Secor, H. V.; Im, H.-S.; Bernstein, E. R. *J. Chem. Soc., Chem. Commun.* **1990**, 87. (d) Breen, P. J.; Bernstein, E. R.; Secor, H. V.; Seeman, J. I. *J. Am. Chem. Soc.* **1989**, *111*, 1958. (e) Seeman, J. I.; Secor, H. V.; Im, H.-S.; Bernstein, E. R. *J. Am. Chem. Soc.* **1990**, *112*, 7073. (f) Li, S.; Bernstein, E. R.; Secor, H. V.; Seeman, J. I. *Tetrahedron Lett.* **1991**, 3945. (g) Shida, N.; Kabuto, C.; Niwa, T.; Ebata, T.; Yamamoto, Y. *J. Org. Chem.* **1994**, *59*, 4068. (h) Ito, M.; Oikawa, A. *J. Mol. Struct.* **1985**, *126*, 133. (i) Oikawa, A.; Abe, H.; Mikami, N.; Ito, M. *Chem. Phys. Lett.* **1985**, *116*, 50. (j) For a review of supersonic jet excitation spectroscopy: Ito, M.; Mikami, N. *Appl. Spectrosc. Rev.* **1980**, *16*, 299.

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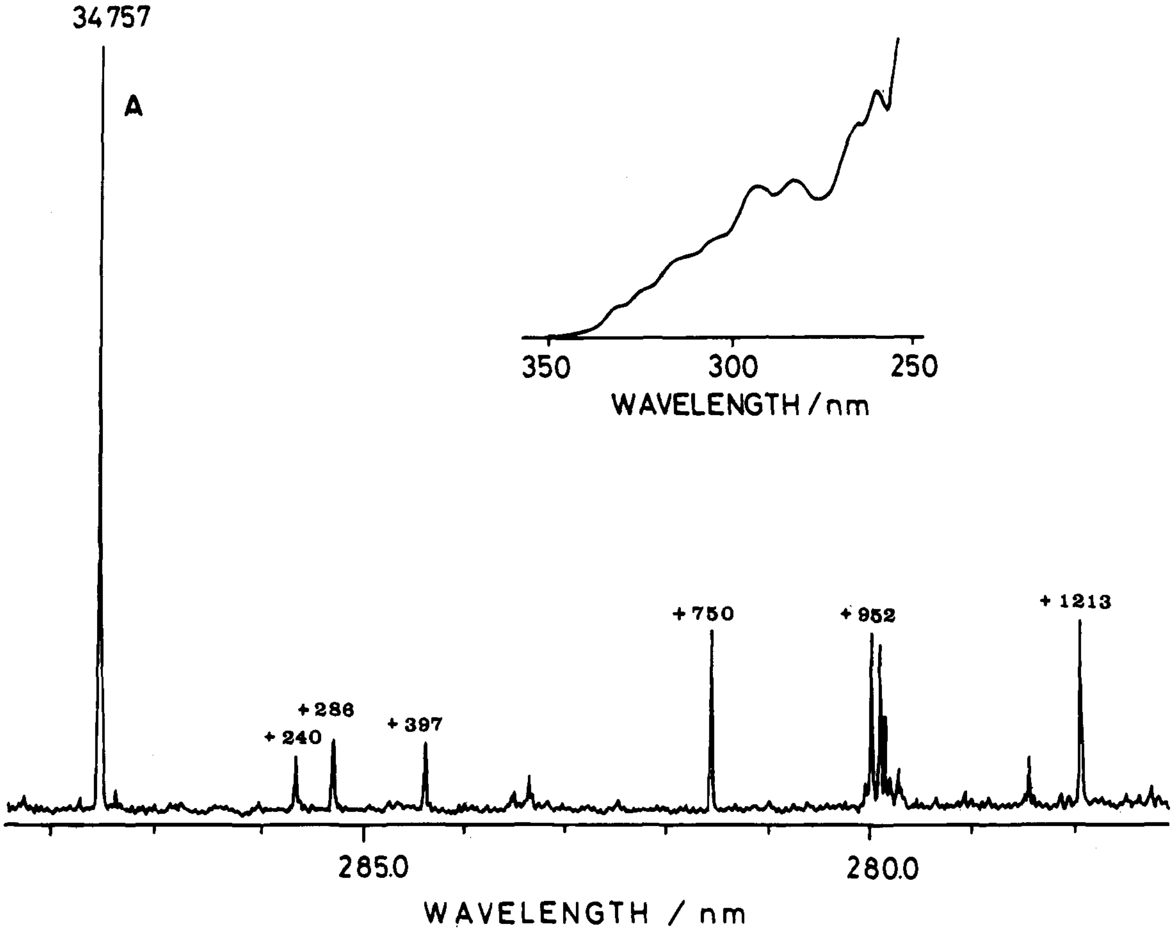
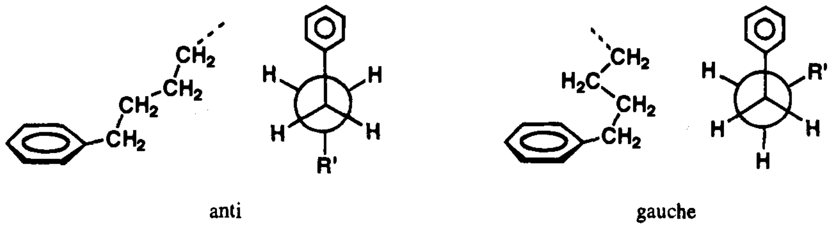


**Figure 1.** Top: absorption spectrum of 2-phenylpropanal in liquid cyclohexane. Bottom: laser-induced fluorescence (LIF) spectrum of jet-cooled 2-phenylpropanal.

**Scheme 1.** Stable Conformers of *n*-Alkylbenzenes



et al.[6a] for the determination of the conformation of *n*-alkylbenzenes (RPh), where the alkyl group is longer than ethyl. They measured the $S_1-S_0$ electronic spectrum of the van der Waals complexes of *n*-alkylbenzenes with He. There exist two stable conformers in *n*-alkylbenzene, anti and gauche (Scheme 1). It was found that though one of the conformers showed the RPh$-$(He)$_2$ band with its spectral red shift twice that of RPh$-$He, the other conformer showed only the RPh$-$He band but not RPh$-$(He)$_2$. It was concluded that the former conformer is the anti form and He atoms are bound on both sides of the benzene ring, while the latter conformer is the gauche form in which the second He cannot be bound on the benzene ring due to steric hindrance with the alkyl group.[6a] We have performed a similar experiment for 2-phenylpropanal by using Ar as a van der Waals partner. As can be seen in Scheme 2, two Ar atoms can be bound on both sides of the benzene ring in conformation **5** but not in conformation **6** due to the steric hindrance with an oxygen atom of the carbonyl group. Figure 3(a) shows the 1 + 1 resonance-enhanced multiphoton ionization (REMPI) spectrum of 2-phenylpropanal, where He was used as a carrier gas, and the spectrum of Figure 3(b) was measured when Ar was used as a carrier gas. As can be seen in the figure, the peaks of 2-phenylpropanal$-$Ar and 2-phenylpropanal$-$(Ar)$_2$ complexes are identified with their red shifts of 32 and 65 cm$^{-1}$, respectively.

Consequently, it is clear that the phenyl and carbonyl group of the stable conformer adopt an antiperiplanar arrangement **5**. The syn arrangement of the di-Ar complex, arising from **3**, is disfavored due to steric crowding as shown in **6**, although both anti and syn (**7** and **8**, respectively) conformers are conceivable in the case of a mono-Ar complex because argon can make a complex at the less hindered side of the aromatic ring. Needless to say, mono and di complexes of intermediate conformers **2** and **4** may be supposed, but here again the di-Ar complexes are disfavored energetically due to the steric repulsion between the argon and carbonyl group. Accordingly, it is concluded

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(6) (a) Hopkins, J. B.; Powers, D. E.; Smalley, R. E. *J. Chem. Phys.* **1980**, *72*, 5039. (b) Reference 5h.

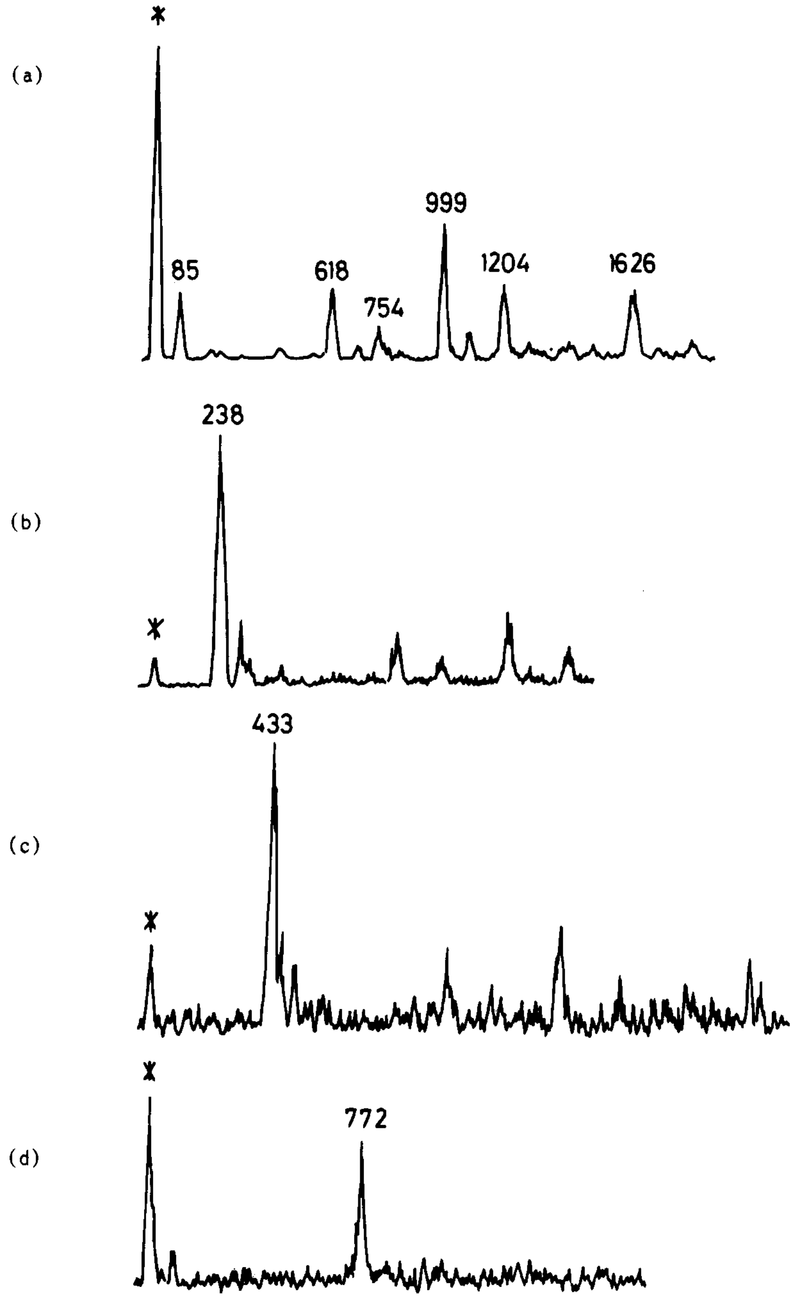
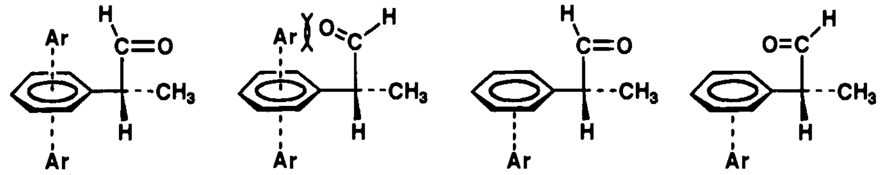


**Figure 2.** Dispersed fluorescence spectra of jet-cooled 2-phenylpropanal obtained by exciting (a) (0,0), (b) (0,0) + 240 cm$^{-1}$, (c) (0,0) + 397 cm$^{-1}$, and (d) (0,0) + 750 cm$^{-1}$ bands. Numbers listed are the vibrational energies in units of cm$^{-1}$.

**Scheme 2.** Di- and Mono-Ar Complexes of 2-Phenylpropanal



anti 5 syn 6 anti 7 syn 8

that 2-phenylpropanal adopts **1** as a single stable conformer in the gas phase. The present study does not tell us anything about the transition state conformations of the aldehyde—nucleophile condensation reactions, but it may be worthwile to compare the ground state conformation obtained experimentally with the proposed transition state geometries.

In Cram's model the only conformer retained is that in which the CO group bisects the included angle defined by the CM and CS bonds; L, M, and S are respectively the large, medium, and small substituents on the chiral center. The major product results from a nucleophilic attack on the side of the small substituent **9**. Karabatsos' model uses the two conformers in

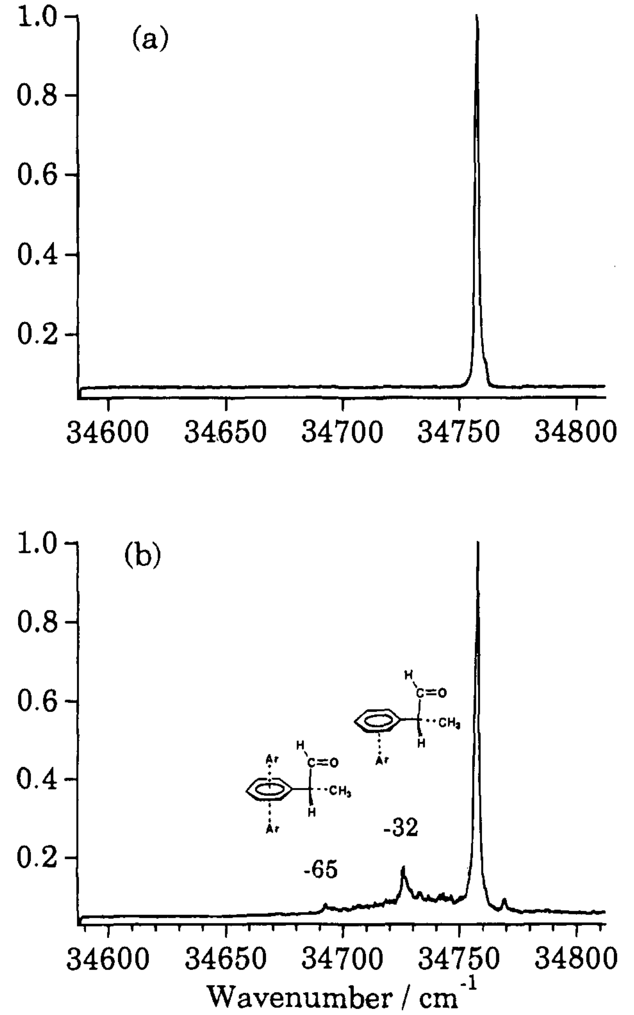
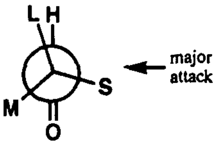


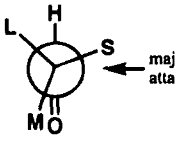
**Figure 3.** 1 + 1 resonance-enhanced MPI spectra of jet-cooled 2-phenylpropanal in the region of band origin. (a) He was used as a carrier gas. (b) Ar was used as a carrier gas. Total ion intensity was monitored.

which the carbonyl group eclipses either the CM or the CL bond (**10** and **11**). In Felkin's model,[7] the favoured transition states are considered to be those where the incipient bond between the carbon atom and the nucleophilic reagent bisects the angle defined by the CM and CS bonds (**12** and **13**). Nonperpendicular attack of nucleophiles is involved in Felkin–Anh model **14**.[3] More recently, computations have shown that the Felkin–Anh model best represents the transition structure for additions of nucleophiles to chiral aldehydes.[8] Very interestingly, the most stable conformer **1** corresponds to the conformer of the transition state considered in Cram's model **9**.



**9**

Cram model



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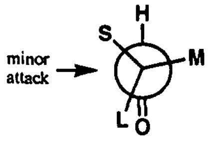

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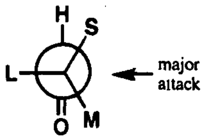
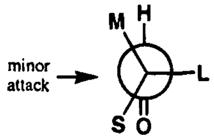
Karabatsos model

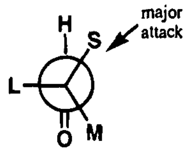


**12**



**13**

Felkin model



**14**

Felkin-Anh model

## Experimental Section

The experimental setup for the measurement of laser-induced fluorescence (LIF) and dispersed fluorescence (DF) spectra of jet-cooled molecules was described elsewhere.[9] 2-Phenylpropanal was heated to 310 K in a nozzle housing to obtain sufficient pressure and seeded in 4 atm of He carrier gas. The seeded gas mixture was expanded into a vacuum chamber through a nozzle having an 800 $\mu$m orifice. The excitation source was from a second harmonics generation of the nitrogen laser-pumped dye laser (Molectron UV24/DL14). The UV output was introduced into a vacuum chamber and crossed the free jet at 15 mm downstream.

The LIF spectrum was measured by monitoring total fluorescence with a photomultiplier tube (Hamamatsu Photonics R-562). The DF spectra from various vibronic levels were measured by using a 0.75 m monochromator (Nalumi) with a photomultiplier tube (Hamamatsu Photonics R-928). Typical spectral resolution was 10 cm$^{-1}$. The signal was amplified by a preamplifier (Par 113) and averaged by a boxcar integrator (Brookdeal 9415/9425). In the measurement of the resonance-enhanced multiphoton ionization (REMPI) spectrum, the generated ions were introduced into a differentially pumped second chamber by an electric field of 20 V/cm and detected by an electron multiplier (Murata Ceratron). In the present experiment, only the total ions were monitored. The ion current was amplified and averaged by the same boxcar integrator system as that of fluorescence measurement.

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