Sheraga (1967). The $\omega$–$\varphi$ energy maps of the three cases showed results approximately similar to one another; the $\omega$–$\varphi$ energy map of Boc-L-Pro-Sar-OBz is shown in Fig. 7. There exist four minimum-energy regions in each of the conformational maps of the three peptides. The differences between the energy minima in the four regions are not significant. Thus, the conformational-energy calculation, although it requires further refinement, shows that for the sarcosyl residue the *cis* peptide bond is able to exist with the same energetical stability as the *trans* peptide bond. The configuration may be mainly determined by the intramolecular interactions with other groups in the molecule and intermolecular forces.

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# The Structure of *tert*-Butoxycarbonyl-L-prolyl-L-isoleucylglycine

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### Abstract

The crystal structure of the title compound was determined by the X-ray method. The space group is $P2_12_12$ with $a = 12{\cdot}909$ (1), $b = 17{\cdot}567$ (2), $c = 10{\cdot}055$ (3) Å and $Z = 4$. The structure was solved by a direct method. In contrast to the $\beta$-turn conformation of a similar sequential peptide Boc-Pro-Leu-Gly-OH, this compound takes an extended conformation to form a dimer structure *via* $\beta$-sheet-type hydrogen bonds. The disordered water on the twofold axis only plays a role as a hydrogen donor.

### Introduction

Among the tripeptides of *N*-(*tert*-butoxycarbonyl)-Pro-*X*-Gly-OH (Boc-Pro-*X*-Gly-OH; *X*: any amino acid residue) type, two compounds, Boc-Pro-Pro-Gly-OH (Hudson, Shaw, Schurr & Jensen, 1972) and Boc-Pro-Leu-Gly-OH (Ashida, Tanaka, Shimonishi & Kakudo, 1977), were studied by the X-ray method, and in the crystalline state an extended conformation was found for the former and a folded or so-called $\beta$-turn conformation for the latter. This structural difference is reasonable in view of the structural role of the prolyl and leucyl residues. The prolyl residue is not expected to be accommodated at the third site of the $\beta$-turn.

The $\beta$-turn conformation is considered to be one of the most important secondary structures in the globular proteins, since it gives a protein its globularity rather than linearity (Chou & Fasman, 1977). Therefore, several peptides of Boc-Pro-*X*-Gly-OH (*X*: Ile, Ala, Val, Met, Phe, *etc.*) were prepared in an attempt to study the effects of various side chains of *X* on the peptide conformations. The present analysis was performed for Boc-Pro-Ile-Gly-OH. Since a forked side

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chain at $C^{\beta}$ of the isoleucyl residue may more severely constrain the structure than the leucyl residue forked at $C^{\gamma}$, it is especially interesting whether Boc-Pro-Ile-Gly-OH can take a $\beta$-turn conformation or not.

## Experimental

### *Sample preparation*

*N*-(*tert*-Butoxycarbonyl)prolylisoleucylglycine was prepared by hydrogenation with a palladium catalyst of Boc-Pro-Ile-Gly-OBzl, which was synthesized by stepwise elongation from the C terminal using *N*,*N*′-dicyclohexylcarbodiimide as a coupling reagent. The elemental analysis of Boc-Pro-Ile-Gly-OH (m.p. 423–425 K) is: found: C 55·98, H 7·80, N 10·92%; calculated for $C_{18}H_{31}N_3O_6.\frac{1}{4}H_2O$: C 55·44, H 8·16, N 10·78%. Later the density measurement and the structure refinement also showed that the crystal contains about a quarter of a water molecule per peptide molecule.

### *Crystallographic experiment*

Single crystals of Boc-Pro-Ile-Gly-OH.$\frac{1}{4}H_2O$ were grown from an ethyl acetate solution as colorless parallelepipeds. Crystal data are: $C_{18}H_{31}N_3O_6.0{\cdot}25H_2O$, $M_r = 389{\cdot}96$, orthorhombic, $P2_12_12$, $a = 12{\cdot}909$ (1), $b = 17{\cdot}567$ (2), $c = 10{\cdot}055$ (3) Å, $U = 2280$ Å$^3$, $D_m = 1{\cdot}138$, $D_x = 1{\cdot}136$ Mg m$^{-3}$, $Z = 4$, $F(000) = 842$.

The crystal used for the X-ray experiment was 0·3 × 0·2 × 0·25 mm. Intensity measurements were made on a Hilger & Watts four-circle diffractometer with Ni-filtered Cu $K\alpha$ radiation. 2421 reflections with $2\theta < 144°$ were collected, 2201 of which were non-zero. Lorentz and polarization factors were applied, but no absorption corrections were made.

## Structure determination

The structure was solved by the direct method with the program *MULTAN* (Germain, Main & Woolfson, 1971). All the 210 normalized structure factors with $|E| > 1{\cdot}4$ were first included in the phase determination, but it was only after eliminating one strong low-angle reflection (001), $|E| = 2{\cdot}8$, that a meaningful $E$ map was obtained.

The parameters were refined by the block-diagonal least-squares program *HBLS* V (Ashida, 1973). In the

Table 1. *The atomic positional parameters* (×10⁴) *with their e.s.d.'s in parentheses*

| | *x* | *y* | *z* |
|---|---|---|---|
| O(1) | 4267 (4) | 2500 (2) | 2116 (4) |
| O(2) | 4097 (4) | 3764 (2) | 1721 (4) |
| O(3) | 6591 (3) | 2195 (2) | 352 (5) |
| O(4) | 6089 (3) | −465 (2) | −937 (5) |
| O(5) | 8159 (3) | −1402 (2) | −1134 (4) |
| O(6) | 7696 (5) | −1817 (2) | −3138 (5) |
| N(1) | 4660 (3) | 2954 (2) | 153 (5) |
| N(2) | 5804 (3) | 1058 (2) | 24(5) |
| N(3) | 7582 (4) | 42 (2) | −1672 (5) |
| C(1) | 4544 (12) | 3074 (7) | 4297 (10) |
| C(2) | 3978 (10) | 1717 (5) | 3928 (11) |
| C(3) | 2773 (8) | 2768 (7) | 3506 (13) |
| C(4) | 3871 (6) | 2531 (4) | 3503 (7) |
| C(5) | 4319 (4) | 3115 (3) | 1345 (7) |
| C(6) | 4796 (4) | 2185 (2) | −420 (6) |
| C(7) | 4841 (7) | 2332 (4) | −1896 (6) |
| C(8) | 5297 (7) | 3149 (4) | −2004 (8) |
| C(9) | 4774 (5) | 3547 (3) | −889 (7) |
| C(10) | 5817 (4) | 1819 (2) | 47 (5) |
| C(11) | 6747 (4) | 614 (2) | 265 (6) |
| C(12) | 6769 (5) | 238 (3) | 1620 (7) |
| C(13) | 6766 (7) | 864 (4) | 2743 (8) |
| C(14) | 7736 (6) | −261 (4) | 1772 (8) |
| C(15) | 6650 (10) | 517 (5) | 4098 (10) |
| C(16) | 6775 (4) | 15 (3) | −836 (6) |
| C(17) | 7642 (5) | −490 (3) | −2763 (7) |
| C(18) | 7835 (5) | −1315 (3) | −2353 (7) |
| O(*W*) | 5000 (0) | 5000 (0) | 3048 (2) |

Table 2. *Hydrogen atom positional parameters* (×10³) *with their e.s.d.'s in parentheses*

| | *x* | *y* | *z* | Bonded to |
|---|---|---|---|---|
| H(1) | 448 (5) | 360 (4) | 398 (7) | C(1) |
| H(2) | 515 (5) | 284 (4) | 411 (7) | C(1) |
| H(3) | 437 (5) | 293 (3) | 498 (7) | C(1) |
| H(4) | 467 (5) | 139 (4) | 384 (6) | C(2) |
| H(5) | 369 (5) | 161 (4) | 505 (6) | C(2) |
| H(6) | 327 (5) | 155 (4) | 332 (6) | C(2) |
| H(7) | 245 (5) | 293 (4) | 448 (7) | C(3) |
| H(8) | 254 (5) | 312 (4) | 310 (7) | C(3) |
| H(9) | 213 (5) | 249 (4) | 276 (7) | C(3) |
| H(10) | 418 (5) | 185 (4) | −27 (7) | C(6) |
| H(11) | 521 (5) | 197 (4) | −238 (7) | C(7) |
| H(12) | 404 (5) | 233 (4) | −235 (7) | C(7) |
| H(13) | 614 (5) | 314 (4) | −185 (7) | C(8) |
| H(14) | 482 (5) | 339 (4) | −281 (6) | C(8) |
| H(15) | 398 (5) | 374 (4) | −122 (7) | C(9) |
| H(16) | 526 (5) | 402 (4) | −48 (7) | C(9) |
| H(17) | 515 (6) | 81 (4) | −26 (6) | N(2) |
| H(18) | 735 (6) | 90 (4) | 17 (7) | C(11) |
| H(19) | 611 (6) | −10 (4) | 171 (6) | C(12) |
| H(20) | 745 (5) | 121 (4) | 270 (7) | C(13) |
| H(21) | 619 (5) | 115 (4) | 261 (7) | C(13) |
| H(22) | 764 (5) | −63 (4) | 122 (7) | C(14) |
| H(23) | 832 (5) | −12 (4) | 136 (6) | C(14) |
| H(24) | 772 (5) | −50 (4) | 278 (7) | C(14) |
| H(25) | 587 (6) | 29 (4) | 390 (7) | C(15) |
| H(26) | 724 (5) | 14 (4) | 431 (6) | C(15) |
| H(27) | 653 (6) | 96 (4) | 482 (7) | C(15) |
| H(28) | 819 (5) | 39 (4) | −198 (6) | N(3) |
| H(29) | 823 (5) | −39 (4) | −357 (7) | C(17) |
| H(30) | 687 (5) | −47 (4) | −343 (7) | C(17) |
| H(31) | 814 (5) | −177 (4) | −88 (7) | O(5) |
| H(32) | 495 (12) | 447 (8) | 241 (14) | O(*W*) |

course of the refinements one significant peak was found on a crystallographic twofold axis in the difference Fourier map. This peak was assigned as a water molecule since its position is appropriate for hydrogen-bond formation with the adjacent peptide, the distance being 2·8 Å. However, the peak was distinctly lower than the expected height, showing the presence of some disordered structures. Its occupancy was estimated as 0·5, *i.e.* one quarter of a molecule for each peptide molecule, and was fixed throughout the refinements.

The atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1974). The final $R$ value was 0·109 for all reflections, and 0·093 for the non-zero reflections. The function minimized was $\sum w(\Delta F)^2$, with $w = 0{\cdot}35567$ for $|F_o| = 0$ and $w = [\sigma^2(F) + 0{\cdot}15433|F_o| - 0{\cdot}00019|F_o|^2]^{-1}$ for $|F_o| > 0$, where $\sigma(F)$ is the standard deviation based on the counting statistics. Three reflections (001, 410 and 220) were excluded from the calculations because they were seriously influenced by the extinction effect. The final positional parameters are listed in Tables 1 and 2.*

## Discussion

Bond lengths, bond angles and torsion angles are shown in Fig. 1(*a*,*b*,*c*). Bond lengths and bond angles are in accordance with the mean values observed in other peptides (Marsh & Donohue, 1967) within experimental errors. The equations of the best planes of several planar groups are listed in Table 3. The crystal structure is shown in Fig. 2 and the hydrogen bonds are listed in Table 4.

### *Main-chain conformation*

As is shown in Fig. 1(*c*), the main chain of this peptide takes an extended form, which contrasts remarkably with the $\beta$-turn form of the similar-sequence peptide Boc-Pro-Leu-Gly-OH (Ashida *et al.*, 1977). This conformational difference is mainly in the torsion angles $\omega_{\text{Boc-Pro}}$, $\psi_{\text{Pro}}$ and $\psi_{\text{Leu}}$ of the Boc–Pro bond and of two $C^{\alpha}$–C′ bonds.

With respect to the Boc–Pro bond, O(1)–C(5)–N(1)–C(6) is *cis* in Boc-Pro-Ile-Gly-OH, but *trans* in Boc-Pro-Leu-Gly-OH (Ashida *et al.*, 1977). In the *N*-substituted amino acid residues, such as prolyl and

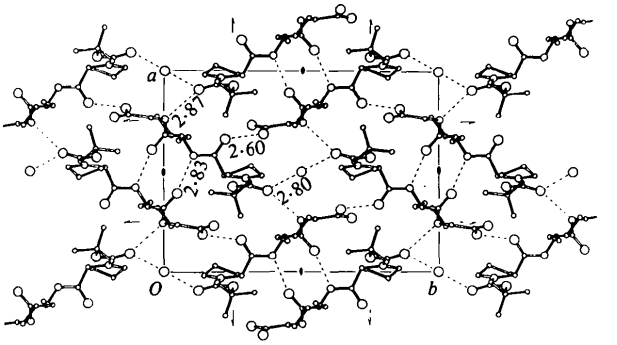


Fig. 2. The crystal structure viewed along the *c* axis. The hydrogen bonds are shown with dashed lines.

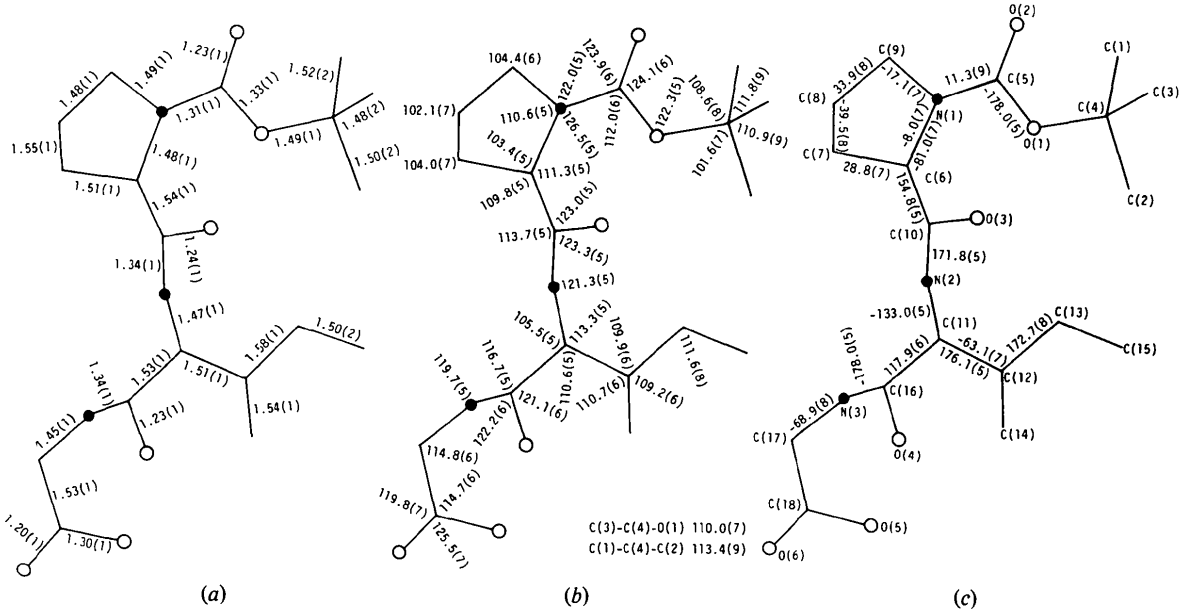


Fig. 1. (*a*) Bond lengths (Å), (*b*) bond angles (°) and (*c*) torsion angles (°).

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34777 (13 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 3. *Best planes*

(*a*) Equations

$X = ax$, $Y = by$, $Z = cz$

| | | |
|---|---|---|
| (I) | $-0.9549X - 0.1130Y - 0.2746Z = -6.3149$ | Boc-Pro amide |
| (II) | $-0.2959X - 0.0299Y + 0.9547Z = -2.2984$ | Pro-Ile peptide |
| (III) | $-0.5176X + 0.6169Y - 0.5928Z = -4.0112$ | Ile-Gly peptide |
| (IV) | $-0.9477X - 0.0782Y + 0.3095Z = -10.1415$ | Gly carbonyl |
| (V) | $0.9036X + 0.4109Y + 0.1207Z = -7.6918$ | Pro ring |
| (VI) | $-0.9815X - 0.0479Y - 0.1852Z = -6.1826$ | (Pro ring) |
| (VII) | $-0.9998X - 0.0107Y - 0.0157Z = -8.7431$ | Ile side chain |

(*b*) Displacements ($\times 10^2$ Å) of atoms from the planes

| (I) | | (II) | | (III) | | (IV) | |
|---|---|---|---|---|---|---|---|
| O(1) | −2 (1) | C(6) | −5 (3) | C(11) | 1 (3) | C(17) | 0 (1) |
| C(5) | 0 (1) | C(10) | 3 (3) | C(16) | 0 (3) | C(18) | 0 (1) |
| O(2) | 4 (1) | O(3) | 0 (3) | O(4) | 0 (3) | O(5) | 0 (1) |
| N(1) | −6 (1) | N(2) | 5 (3) | N(3) | 1 (3) | O(6) | 0 (1) |
| C(6) | 9 (1) | C(11) | −5 (3) | C(17) | 2 (3) | | |
| C(9) | −3 (1) | | | | | | |
| (V) | | (VI) | | (VII) | | | |
| N(1) | −10 (1) | N(1) | 0 | C(11) | 2 (1) | | |
| C(6) | −57 (1) | C(6) | 0 | C(12) | −2 (1) | | |
| C(7) | −58 (1) | C(9) | 0 | C(13) | −5 (2) | | |
| C(8) | 51 (1) | C(8)* | −42 (2) | C(15) | 8 (2) | | |
| C(9) | 33 (1) | C(7)* | 20 (2) | C(16)* | 1 (1) | | |
| C(10) | 41 (1) | C(10)* | −135 (1) | | | | |

* Atoms not included in the calculations of the planes.

Table 4. *Hydrogen-bond distances*

| Donor | Acceptor | |
|---|---|---|
| O(5) | O(3)$^{i}$ | 2·60 (1) Å |
| N(2) | O(4)$^{ii}$ | 2·83 (1) |
| N(3) | O(2)$^{iii}$ | 2·87 (1) |
| O(*W*) | O(2) | 2·80 (3) |

Symmetry code

(i) $1.5 - x, -0.5 + y, -z$ (iii) $0.5 + x, 0.5 - y, z$

(ii) $1.0 - x, -y, z$

sarcosyl, the *cis* form is more stable than the *trans* (Itoh, Yamane, Ashida, Sugihara, Imanishi & Higashimura, 1976), and the energy loss due to taking the *trans* form in Boc-Pro-Leu-Gly-OH (Ashida *et al.*, 1977) may be compensated by the formation of the intramolecular hydrogen bond between C=O in the Boc group and N–H of the glycyl residue. The carbonyl O atom of the Boc group in the present peptide participates in the intermolecular hydrogen bond.

The difference in the torsion angles of $C^{\alpha}$–C′ ($\psi$) is obvious when the values in Fig. 1(*c*) are compared with the corresponding values of the Boc-Pro-Leu-Gly-OH (Ashida *et al.*, 1977) for Pro ($\varphi = -65.0$, $\psi = -20.7°$) and for Leu ($\varphi = -110.8$, $\psi = 26.7°$).

According to the study by Chou & Fasman (1977), who investigated the $\beta$-turn in many proteins, the potential for Pro and Gly to occupy the second and fourth site of the $\beta$-turn is very high, whereas the potential for Leu and Ile to occupy the third site is very low since the third site sticks out of the molecular surface which is in a hydrophilic environment. Nevertheless, in peptides, the preference of the -Pro-Leu-Gly- sequence for the $\beta$-turn conformation seems to be obvious when one looks at the $\beta$-turn structure of Boc-Pro-Leu-Gly-OH (Ashida *et al.*, 1977), together with the same structure observed in similar peptides.

The different conformation observed in Boc-Pro-Ile-Gly-OH, on the other hand, suggests the different structural role of the isoleucyl residue. The side chain forked at $C^{\beta}$ influences the main-chain conformation, resulting in an extended structure. Thus, isoleucine is not likely to occupy the third site of the $\beta$-turn because the forked structure at $C^{\beta}$ places a stereochemical restriction on the main-chain folding.

The extended conformation of the present peptide is stabilized mainly by the two intermolecular N–H···O hydrogen bonds of 2·83 Å, in a similar way to the antiparallel $\beta$-sheet hydrogen bonds. The torsion angles ($\varphi$,$\psi$) of Ile (−133, 117·9°) are nearly intermediate between those (−139, 135°) for the antiparallel $\beta$ sheet (Arnott, Dover & Elliott, 1967) and those (−119, 113°) for the parallel $\beta$ sheet (Schellman & Schellman, 1964).

### *Side-chain conformation*

In the isoleucyl residue the conformation about the $C^{\beta}$–$C^{\gamma_1}$ bond [C(11)–C(12)–C(13)–C(15)] is *trans*. This conformation has been observed in L-isoleucine (Torii & Iitaka, 1971) and L-isoleucine.HCl.$H_2O$ (Trommel & Bijvoet, 1954; Weeks, Cooper & Norton, 1969). Also, $C^{\gamma_1}$ is *trans* to C′ in terms of the $C^{\alpha}$–$C^{\beta}$ bond; therefore, C′–$C^{\alpha}$–$C^{\beta}$–$C^{\gamma_1}$–$C^{\delta}$ [C(16)–C(11)–C(12)–C(13)–C(15)] is planar and *trans*-zigzag. The displacement of C(16) from the best plane for C(11), C(12), C(13) and C(15) is 0·02 Å. In most of the leucyl residues in peptides, C′–$C^{\alpha}$–$C^{\beta}$–$C^{\gamma}$–($C^{\delta_1}$ or $C^{\delta_2}$) is usually *trans*-zigzag (Sugino, Tanaka & Ashida, 1978). These facts suggest that the branched side chain also tends to form a *trans*-zigzag conformation.

In the prolyl residue the displacements of C(7), C(8) and C(10) from the plane of N(1), C(6) and C(9) are shown in Table 3. The conformation of the ring is $C_2$–$C^{\gamma}$-*endo*, following the notation of Ashida & Kakudo (1974).

### *Role of water*

The water molecule on the twofold axis only plays a role as a hydrogen donor in hydrogen bonding with the carbonyl O of the Boc group. The function of this water seems to be that of space filling, as in H-Leu-Pro-Gly-OH (Leung & Marsh, 1958) and H-Gly-Phe-Gly-OH (Marsh & Glusker, 1961). It is worth mentioning that in all these three crystals the water molecules are only involved as donors in hydrogen bonding and have small non-stoichiometric occupancy factors [0·5 in the present crystal and H-Gly-Phe-Gly-OH (Marsh &

Glusker, 1961) and 0·8 in H-Leu-Pro-Gly-OH (Leung & Marsh, 1958)]. The role of water molecules as hydrogen-bond donors seems to be less important than that as hydrogen-bond acceptors. This is because potential hydrogen-bond acceptors not accepting a bond are very common, but potential hydrogen-bond donors (OH or NH) not participating in hydrogen bonds are rarely found in crystals. In the latter case the role of water as an acceptor seems to be important.

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# The Structure of 3-(2-Methoxyphenyl)-1,1,2,2-cyclopropanetetracarbonitrile

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## Abstract

Crystals of $C_{14}H_8N_4O$ are monoclinic, space group $P2_1$. Unit-cell constants are $a = 13{\cdot}241\ (4)$, $b = 7{\cdot}446\ (2)$, $c = 6{\cdot}436\ (2)$ Å, $\beta = 93{\cdot}23\ (2)°$. $V = 633{\cdot}5$ Å$^3$, $Z = 2$, $D_{obs} = 1{\cdot}30$ (flotation), $D_{calc} = 1{\cdot}300$ Mg m$^{-3}$ and $\mu$(Cu $K\alpha$) = 0·72 mm$^{-1}$. The structure, solved by direct methods, has been refined to an $R$ value of 3·5% using 1245 intensity measurements. The combined effect of electron-withdrawing and -donating substituents on the geometry of the cyclopropane ring is discussed.


## Introduction

The cyclopropane ring undergoes drastic geometrical changes under the influence of electron-withdrawing and -donating substituents. According to Walsh (1947, 1949), trigonal methylene groups are brought together to form the ring by overlap of their $\sigma$ orbitals at the center and of their $p$ or $\pi$ orbitals around the periphery (Fig. 1). The three $\sigma$ orbitals combine to produce a strongly bonding $A_1'$ level and an antibonding $E'$ pair (degenerate). The three methylene $p$ orbitals interact less strongly to yield a bonding $E'$ pair and an antibonding $A_2'$ level. The resulting orbitals, shown in Fig. 2, are reproduced from Jorgensen & Salem (1973). The

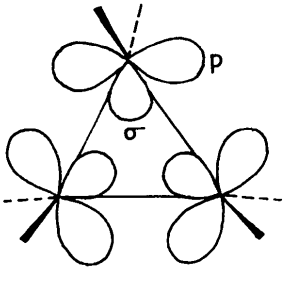


Fig. 1. The Walsh model.

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