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# Structure and Crystal Packing of the Organic Salt 2-(Dimethylamino)-5-methyl-1,3-thiazolium 1,1,2,3,3-Pentacyanopropenide, $C_6H_{11}N_2S^+.C_8N_5^-$

By Valerio Bertolasi and Gastone Gilli

*Centro di Strutturistica Diffrattometrica, University of Ferrara, Italy*

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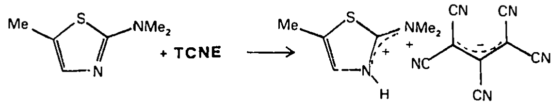
**Abstract.** $(DMAT)^+.$ $(PCP)^-$, $M_r = 309{\cdot}3$, $Pna2_1$, $a = 31{\cdot}159\ (4)$, $b = 8{\cdot}486\ (4)$, $c = 5{\cdot}793\ (2)$ Å, $V = 1531\ (1)$ Å$^3$, $Z = 4$, $D_x = 1{\cdot}34$ Mg m$^{-3}$, $\lambda(\mathrm{Cu}\ K\alpha) = 1{\cdot}54178$ Å, $\mu(\mathrm{Cu}\ K\alpha) = 1{\cdot}83$ mm$^{-1}$, $F(000) = 640$, $T = 298$ K, $R = 0{\cdot}045$ for 1197 observed reflections ($3\sigma$ level). $(DMAT)^+.(PCP)^-$ ion pairs are connected by hydrogen bonds and lie on a common plane inclined by 37° to the $(a,c)$ plane. Along **b** the structure consists of an infinite stack where the cation is sandwiched by anions and *vice versa*. Geometrical considerations and the symmetry of the frontier molecular orbitals indicate the presence of a $\pi$–$\pi^*$ charge-transfer interaction linking the ions in couples inside the stack. The geometries of the anion and cation are discussed.

**Introduction.** The $(DMAT)^+.$ $(PCP)^-$ organic salt was obtained by reacting 2-(dimethylamino)-5-methyl-1,3-thiazole with tetracyanoethylene (TCNE). A possible reaction mechanism leading to the observed product has already been discussed (Medici, Pedrini, Venturoli & Dondoni, 1981) and a general account on the formation of this kind of anion by basic hydrolysis of TCNE has been given by Middleton, Little, Coffman & Engelhardt (1958). The present paper reports the first example of such salts in the thiazole series and the first unquestionable molecular structure determination of the PCP ion, which in the only previous investigation (Sim, Woodhouse & Knox, 1979) was found to be disordered.



**Experimental.** Deep-yellow prism, $0{\cdot}15 \times 0{\cdot}20 \times 0{\cdot}50$ mm, automatic Siemens AED diffractometer, Ni-filtered Cu $K\alpha$, $\omega/2\theta$ scan ($\theta \leq 60°$), 1261 independent reflections, $h$ 0–34, $k$ 0–9, $l$ 0–6, 1197 having $I > 3\sigma(I)$ observed, no absorption correction, direct methods [*MULTAN*74 (Main, Woolfson, Lessinger, Germain & Declercq, 1974)], full-matrix least-squares refinement on $F$, anisotropic for all non-H atoms, *SHELX*76 (Sheldrick, 1976), methyl H's given calculated positions, others refined isotropically, scattering factors from *International Tables for X-ray Crystallography* (1974), $1/w = \sigma^2_{Fo} + 0{\cdot}011\,|F_o|^2$, discrepancy factors $R = 0{\cdot}045$, $R_w = \sum w^{1/2}|\Delta|/\sum w^{1/2}|F_o| = 0{\cdot}048$, maximum shift/error = 0·34, final difference Fourier map rather flat with maxima smaller than 0·25 e Å$^{-3}$.*

**Discussion.** Final atomic positional parameters are given in Table 1.

A view of the molecule projected on the mean plane of the anion is reported in Fig. 1. Bond distances and angles and a selection of torsion angles are reported in

Table 1. *Positional* ($\times 10^4$) *and thermal* (Å$^2$ $\times 10^3$) *parameters with e.s.d.'s in parentheses*

$$U_{eq} = \tfrac{1}{3}\textstyle\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

| | $x$ | $y$ | $z$ | $U_{eq}/U$ |
|---|---|---|---|---|
| S | 3800·7 (2) | 4902 ·3 (9) | 2761 | 40·0 (5) |
| C(1) | 3559 (1) | 5718 (4) | 5184 (7) | 38 (2) |
| C(2) | 4250 (1) | 6629 (4) | 5401 (8) | 44 (2) |
| C(3) | 4294 (1) | 5802 (4) | 3446 (7) | 41 (2) |
| C(4) | 2966 (1) | 6256 (6) | 7763 (11) | 66 (2) |
| C(5) | 2865 (1) | 4617 (6) | 4242 (10) | 60 (3) |
| C(6) | 4670 (1) | 5621 (5) | 1908 (9) | 56 (2) |
| N(1) | 3843 (1) | 6584 (4) | 6343 (7) | 44 (2) |
| N(2) | 3158 (1) | 5474 (4) | 5756 (7) | 49 (2) |
| H(N1) | 3743 (12) | 7186 (55) | 7392 (109) | 59 (13) |
| H(2) | 4432 (11) | 7181 (35) | 6060 (61) | 23 (8) |
| C(7) | 4163 (1) | 10492 (4) | 13440 (7) | 42 (2) |
| C(8) | 4605 (1) | 10929 (4) | 13262 (8) | 51 (2) |
| C(9) | 4012 (1) | 9514 (4) | 11624 (8) | 44 (2) |
| C(10) | 3909 (1) | 11045 (4) | 15194 (8) | 41 (2) |
| C(11) | 4117 (1) | 12072 (4) | 16864 (8) | 48 (2) |
| C(12) | 3474 (1) | 10767 (4) | 15663 (8) | 45 (2) |
| C(13) | 3215 (1) | 9736 (5) | 14319 (11) | 55 (2) |
| C(14) | 3274 (1) | 11488 (5) | 17635 (11) | 58 (2) |
| N(3) | 4962 (1) | 11270 (5) | 13097 (10) | 76 (2) |
| N(4) | 3893 (1) | 8741 (4) | 10148 (8) | 59 (2) |
| N(5) | 4266 (1) | 12901 (5) | 18202 (8) | 68 (2) |
| N(6) | 2999 (1) | 8888 (5) | 13317 (10) | 79 (3) |
| N(7) | 3115 (1) | 12095 (6) | 19168 (11) | 83 (3) |

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38606 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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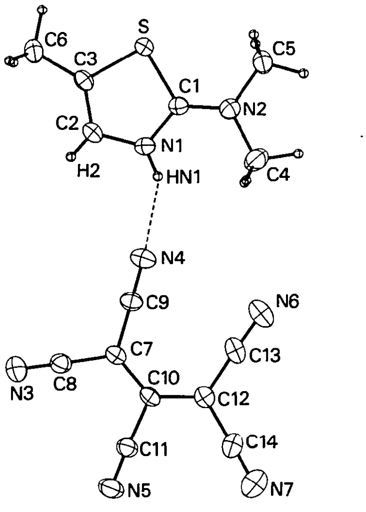


Fig. 1. An *ORTEP* (Johnson, 1971) view of the ion pair projected on the mean plane of the anion.

Table 2. *Interatomic distances* (Å), *bond angles* (°) *and a selection of torsion angles* (°) *with e.s.d.'s in parentheses*

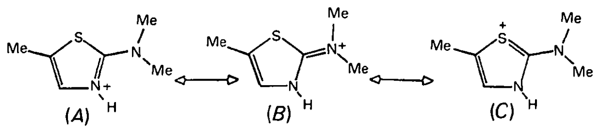
| | | | |
|---|---|---|---|
| S—C(1) | 1·737 (4) | C(7)—C(10) | 1·370 (6) |
| S—C(3) | 1·762 (3) | C(8)—N(3) | 1·155 (5) |
| C(1)—N(1) | 1·333 (5) | C(9)—N(4) | 1·139 (6) |
| C(1)—N(2) | 1·309 (4) | C(10)—C(11) | 1·454 (5) |
| C(2)—N(1) | 1·381 (5) | C(10)—C(12) | 1·405 (5) |
| C(2)—C(3) | 1·340 (6) | C(11)—N(5) | 1·145 (5) |
| C(2)—H(2) | 0·83 (4) | C(12)—C(13) | 1·421 (6) |
| C(3)—C(6) | 1·480 (6) | C(12)—C(14) | 1·437 (7) |
| C(4)—N(2) | 1·466 (6) | C(13)—N(6) | 1·145 (6) |
| C(5)—N(2) | 1·460 (6) | C(14)—N(7) | 1·141 (7) |
| N(1)—H(N1) | 0·85 (6) | N(4)···N(1) | 2·869 (6) |
| C(7)—C(8) | 1·429 (5) | N(4)···H(N1) | 2·12 (6) |
| C(7)—C(9) | 1·421 (5) | | |

| | | | |
|---|---|---|---|
| C(1)—S—C(3) | 91·4 (2) | C(4)—N(2)—C(5) | 116·5 (3) |
| S—C(1)—N(1) | 109·7 (3) | C(8)—C(7)—C(9) | 114·7 (3) |
| S—C(1)—N(2) | 123·8 (3) | C(8)—C(7)—C(10) | 121·3 (3) |
| N(1)—C(1)—N(2) | 126·5 (4) | C(9)—C(7)—C(10) | 123·9 (3) |
| C(3)—C(2)—N(1) | 114·4 (3) | C(7)—C(8)—N(3) | 179·2 (4) |
| C(3)—C(2)—H(2) | 128 (2) | C(7)—C(9)—N(4) | 179·1 (4) |
| N(1)—C(2)—H(2) | 117 (2) | C(7)—C(10)—C(11) | 116·2 (3) |
| S—C(3)—C(2) | 109·2 (3) | C(7)—C(10)—C(12) | 130·0 (3) |
| S—C(3)—C(6) | 120·7 (3) | C(11)—C(10)—C(12) | 113·7 (4) |
| C(2)—C(3)—C(6) | 130·1 (3) | C(10)—C(11)—N(5) | 177·5 (4) |
| C(1)—N(1)—C(2) | 115·3 (3) | C(10)—C(12)—C(13) | 123·0 (4) |
| C(1)—N(1)—H(N1) | 117 (3) | C(10)—C(12)—C(14) | 120·0 (3) |
| C(2)—N(1)—H(N1) | 127 (3) | C(13)—C(12)—C(14) | 116·9 (3) |
| C(1)—N(2)—C(4) | 121·2 (3) | C(12)—C(13)—N(6) | 177·2 (6) |
| C(1)—N(2)—C(5) | 121·6 (3) | C(12)—C(14)—N(7) | 178·2 (4) |

| | | | |
|---|---|---|---|
| S—C(1)—N(2)—C(5) | −6·8 (5) | C(9)—C(7)—C(10)—C(12) | 2·4 (4) |
| N(1)—C(1)—N(2)—C(4) | 4·1 (6) | C(7)—C(10)—C(12)—C(13) | 2·6 (6) |
| C(8)—C(7)—C(10)—C(11) | −1·0 (5) | C(11)—C(10)—C(12)—C(14) | 0·6 (5) |

Table 2. The thiazole molecule is protonated at the imino N(1) atom and the crystal contains pairs connected by the hydrogen bond N(1)—H(N1)···N(4) [N(1)···N(4) = 2·869 (6), H(N1)···N(4) = 2·12 (6) Å].

The thiazolium ring is planar within experimental error ($\chi^2 = 2{\cdot}1$). The —NMe$_2$ group lies approximately in this plane as indicated by the N(1)—C(1)—N(2)—C(4) torsion angle of 4·1 (6)°. Comparison of bond distances with those of thiazole (determined by microwave spectroscopy; Nygaard *et al.*, 1971) and other thiazole derivatives (Caranoni & Reboul, 1982, and references therein) shows that the cooperative effect of dimethylamino substitution and protonation reduces the aromatic character of the thiazole ring by resonance among the canonical forms.



Accordingly, the C(2)—C(3), S—C(3) bond distances of 1·340 (6) and 1·762 (3) Å fit better with the estimated $C_{sp^2}{=}C_{sp^2}$ [1·33 Å] and S—$C_{sp^2}$ (1·76 Å; Sacerdoti, Bertolasi, Gilli, Dondoni & Battaglia, 1977) distances than with the values found in 1,3-thiazole [1·367 (1) and 1·713 (1) Å respectively]. Here the polar form (*B*), strongly stabilized by the protonation of the imino nitrogen, gives the shortest $C_{sp^2}$—NMe$_2$ distance ever observed (Gilli & Bertolasi, 1979, 1981). The resonance in the amidino group reduces the contribution of polar form (*C*), as can be seen by the fact that the S—C(1) distance of 1·737 (4) Å is much longer than that found in 2-alkyl substituted 1,3-thiazolium ions (1·68 Å as estimated, on average, by Caranoni & Reboul, 1982). As regards bond angles, protonation is seen to cause a widening of the C(1)—N(1)—C(2) angle of 5·2 (4)° with respect to that of 1,3-thiazole [110·1 (1)°]. The effect is confirmed by other 3-alkyl substituted 1,3-thiazolium ions and can be interpreted within the VSEPR theory (Gillespie, 1972) by the reduced space taken by the nitrogen lone pair after protonation (Bertolasi, Sacerdoti, Gilli & Borea, 1982).

The PCP anion is roughly planar. The C(7)—C(10) and C(10)—C(12) distances of 1·370 (6) and 1·405 (5) Å are intermediate between double- and single-bond distances according to the resonance $\rangle C^{-}-\overset{|}{C}=C\langle \longleftrightarrow \rangle C=\overset{|}{C}-{}^{-}C\langle$ and to the other structures of similar anions (Tamamura, Yamane, Yasuoka & Kasai, 1974; Klewe, 1971; Edmonds, Herdklotz & Sass, 1970). The ion is not fully symmetric. The main asymmetry arises from the difference of 0·035 (7) Å between the two central C—C bonds, all angular distortion being derived from that through the rule that angles opposed to shorter bonds are narrower. However, the shortening of the C(7)—C(10) distance cannot be connected with the influence of the N(1)···N(4) hydrogen bond within the framework of valence-bond theory. It might be related to the intermolecular charge transfer discussed below but no proof can be given.

The crystal packing along **b** is shown in Fig. 2 and the shortest intermolecular distances are given in Table 3. The packing consists of ion pairs arranged along **c** linked by N(1)—H(N1)···N(4) hydrogen bonds. The least-squares planes through the cation and the anion

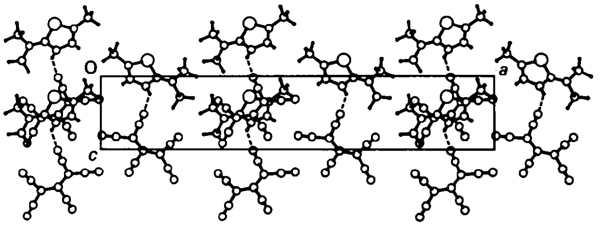


Fig. 2. The crystal structure projected along **b**.

## Table 3. *Short intermolecular distances* (Å)

Average e.s.d. is 0·006 Å. Calculated values are taken from Bondi (1964) assuming $r_w(S) = 1·80$, $r_w(C_{sp}) = 1·78$, $r_w(C_{sp^2}) = 1·70$, $r_w(N_{sp}$, perpendicular$) = 1·70$, $r_w(N_{sp}$, parallel$) = 1·40$, $r_w(N_{sp^2}) = 1·55$ Å.

(*a*) Contacts within ions stacked in columns (Figs. 2–4)

| | Observed | Calculated |
|---|---|---|
| $C(1^i)\cdots N(6^{ii})$ | 3·383 | 3·40 |
| $C(2^i)\cdots C(7^{ii})$ | 3·480 | 3·40 |
| $C(2^i)\cdots C(9^{ii})$ | 3·367 | 3·48 |
| $C(3^i)\cdots C(9^{ii})$ | 3·437 | 3·48 |
| $C(3^i)\cdots N(4^{ii})$ | 3·381 | 3·40 |
| $N(2^i)\cdots N(6^{ii})$ | 3·261 | 3·25 |
| $S^i\cdots C(10^{iii})$ | 3·580 | 3·50 |
| $S^i\cdots C(11^{iii})$ | 3·520 | 3·58 |

(*b*) Closest contacts between columns caused by the hydrogen bond N(1)···N(4)

| | Observed | Calculated |
|---|---|---|
| $N(1^i)\cdots N(4^i)$ | 2·869 | 2·80 |
| $N(4^i)\cdots C(12^{ii})$ | 3·378 | 3·40 |
| $N(4^i)\cdots C(14^{ii})$ | 3·357 | 3·48 |

Symmetry code: (i) $x, y, z$; (ii) $x, y, z-1$; (iii) $x, y-1, z-1$.

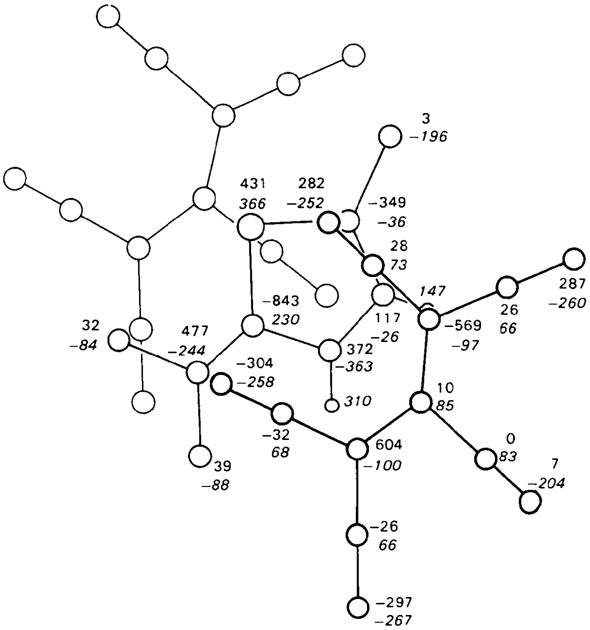


Fig. 3. A projection on the best cation plane of a section of column where cations and anions stack alternately along **b**. Symmetry operations are $(x,y,z)$ for the cation, $(x,y,z-1)$ for the upper anion and $(x,y-1,z-1)$ for the lower one. Figures refer to the coefficients of the atomic $p_z$ orbitals ($\times 10^3$) for HOMO of the anion and LUMO of the cation and (in italic) to the net atomic charges ($\times 10^3$), both calculated by *ab initio* methods.

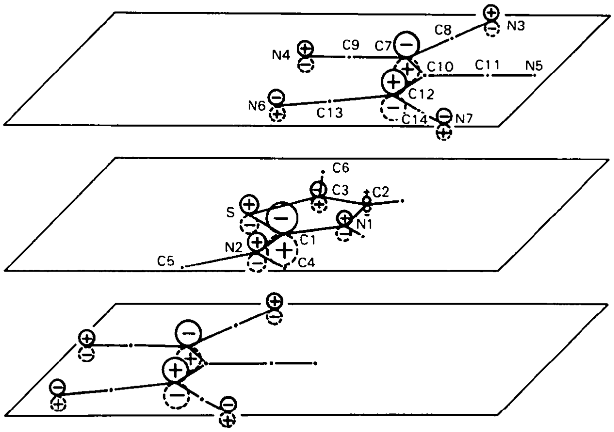


Fig. 4. Axonometry of Fig. 3. The $p_z$ atomic orbitals have sizes proportional to their HOMO and LUMO coefficients.

form an angle of only 1·12 (7)° and are inclined to the (*a*,*c*) plane at 36·51 (6) and 37·55 (3)°, respectively, climbing upwards or downwards for couples of ions situated at $x$ and $x + 1/2$ or $x + 1/4$ and $x + 3/4$, alternately. Along **b** the structure is built up by parallel infinite columns where the cations and anions stack alternately. In each column the cation is sandwiched by anions (and *vice versa*). Fig. 3 shows the projection on the best cation plane of a section of such a column and Fig. 4 reports its axonometry perpendicular to this plane. The cation has closer contacts with the upper anion than the lower one, the mean interplanar distance being 3·33 (1) and 3·47 (1) Å for the former and the latter, respectively. As the cation is not equidistant from the two anions, each column can be considered as built up of parallel-faced couples of ions as smaller stacking units.

The reason for the formation of such 'faced couples of ions' may be sought in a better $\pi$–$\pi^*$ charge-transfer interaction inside the dimer, that is in the fact that the lower unoccupied molecular orbital (LUMO) of the cation overlaps better with the higher occupied molecular orbital (HOMO) of the upper anion than with that of the lower one (Figs. 3,4). In Fig. 3 are reported the values of the $p_z$ atomic orbitals in the HOMO of the PCP anion and the LUMO of the DMAT cation. In the same figure are reported values for net atomic charges for both ions. Calculations were performed by standard *ab initio* LCAO SCF methods using the *GAUSSIAN*76 (Pople *et al.*, 1978) system of programs and the STO-3G basis set. In Fig. 4 are shown the shapes of the HOMO of the anion and LUMO of the cation. From a qualitative point of view, the overlapping seems to be geometrically favoured and symmetry-allowed for the N(6)→N(2), N(4)→C(3) and C(7)→C(2) couples of atoms, where the arrows indicate the direction of the hypothetical intermolecular charge transfer. All these interactions occur between the cation and the upper anion of Figs. 3 and 4, supporting the hypothesis of the stacking of charge-transfer dimers. Conversely, no $\pi$ overlap can occur between the cation and the underlying anion as the S atom, the only one with suitably short contacts, is almost exactly situated over the nodal line through C(10), C(11) and N(5) of the HOMO of the anion. A similar arrangement has been already found by Tamamura *et al.* (1974) in the organic charge-transfer salt between 1,1,3,3-tetracyanopropenide (an anion strictly similar to the present one) and 2,4,6-triphenylpyrylium.

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# Structure of Methyl 10-Ethyldicyclohepta[*cd,gh*]pentalene-5-carboxylate, $C_{20}H_{16}O_2$

BY CHIZUKO KABUTO, KIYOSHI FUJIMORI, MASAFUMI YASUNAMI AND KAHEI TAKASE
*Department of Chemistry, Faculty of Science, Tohoku University, Sendai* 980, *Japan*

AND NOBORU MORITA AND TOYONOBU ASAO
*Department of Chemistry, College of General Education, Tohoku University, Sendai* 980, *Japan*

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**Abstract.** $M_r = 288\cdot35$, monoclinic, $P2_1/n$, $a = 11\cdot339\ (2)$, $b = 13\cdot423\ (2)$, $c = 10\cdot485\ (1)$ Å, $\beta = 113\cdot80\ (2)°$, $V = 1460\cdot14$ Å$^3$, $D_x = 1\cdot31$ for $Z = 4$, $D_m = 1\cdot19$ g cm$^{-3}$, $F(000) = 608$, Mo $K\alpha$ radiation. diffractometer data ($\lambda = 0\cdot71069$ Å, graphite monochromator), $\mu = 0\cdot78$ cm$^{-1}$, room temperature. The final $R$ factor is 0·073 for the 2563 observed reflections. The molecular skeleton shows a completely planar and $14\pi$ peripheral aromatic structure in good agreement with the theoretical prediction. The crystal structure consists of a pair of molecules almost parallel with each other with contacts corresponding to the shorter limits of the van der Waals distances.

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**Introduction.** There are known to exist three nonalternant pyrene isomers fused with only five- and seven-membered rings, dicyclohepta[*cd,gh*]pentalene (1) (Reel & Vogel, 1972), dicyclopenta[*ef,kl*]heptalene (2) (Anderson, MacDonald & Montana, 1968; Jutz & Schweiger, 1971), and pentaleno[6,1,2-*def*]heptalene (3) (Hafner, Fleischer & Fritz, 1965). These types of polycyclic conjugated hydrocarbons are of special interest for their characterization of the $14\pi$ peripheral aromatic system, as predicted from quantum mechanical MO calculations (Zahradnik, 1965; Zahradnik, Michel & Pancir, 1966; Toyota & Nakajima, 1973).