

Unless otherwise specified, all the programs referred to in this paper have been used in their VAX VMS versions of the CCP4 suite of crystallographic programs (SERC Daresbury Laboratory, 1986). XPLOR Version 1.5 as obtained from A. T. Brunger was used on a CRAY X-MP/416 supercomputer (SERC Rutherford Appleton Laboratory).

Novo-Nordisk Industri A/S, Copenhagen, Denmark, and the European Economic Community (Bridge Program) are thanked for financial support; the Protein Crystallography Group in York is also financed by a consolidated grant from the SERC (UK), who are also acknowledged for the provision of the CRAY computing time. JPT gratefully acknowledges a studentship under the EEC Biotechnology Action Program. The preparation of the final version of this paper took place at the University of Alberta, Edmonton, where ZSD is financed by an MRC (Canada) grant to the Group in Protein Structure and Function.

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*Acta Cryst.* (1992). **B48**, 319–324

## Model Deformation Density Studies of Tetraethylthiuram Disulfide

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(Received 21 October 1991; accepted 13 January 1992)

#### Abstract

The title compound, tetraethylthiuram disulfide,  $C_{10}H_{20}N_2S_4$ , was studied by X-ray diffraction at 105 K. Crystal data:  $P2_1/c$ ,  $a = 10.922$  (3),  $b = 15.946$  (4),  $c = 8.444$  (1) Å,  $\beta = 91.92$  (1)°,  $Z = 4$ . The bonding character of this molecule was examined by means of the deformation density distribu-

tion both in a multipole expansion model and in a theoretical calculation according to the extended Hückel molecular orbital method. The deformation density distribution, after multipole refinements, shows clear features in both the bonding and lone-pair electron regions. Positive deformation density is found along the C—C, C—N and C—S bonds. There is very little density along the S—S bonds. The net atomic charges obtained from both methods are discussed.

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### Introduction

The electron density of tetraethylthiuram disulfide has been studied experimentally (Wang & Liao, 1989). In order to obtain further information about the bonding character of this compound, we calculated the deformation electron density based on the multipole expansion model (Hansen & Coppens, 1978) and the extended Hückel approximation (Howell, Rossi, Wallace, Haraki & Hoffmann, 1977). The multipole model is expressed as a series expansion of spherical harmonic terms ( $Y_{lm}$ ) multiplied by a Slater-type radical function  $R_l(r)$ , such as

$$\sum_{l=0}^4 R_l(r) \sum_{m=-l}^{+l} P_{lm} Y_{lm}$$

where

$$R_l(r) = \frac{\zeta^{n_l+3}}{(n_l+2)!} r^{n_l} \exp(-\zeta r)$$

and  $P_{lm}$  are the multipole coefficients which are determined by least-squares refinement. The molecular geometry for the theoretical calculation was taken from the low-temperature diffraction data of the previous study (Wang & Liao, 1989). The experimental  $X$ - $X$  deformation maps normally suffered from a high noise level (Wang, Wu & Cheng, 1990). The multipole deformation maps should give much clearer features and possibly more meaningful information about bonding than the experimental ones. With the comparison of corresponding theoretical deformation maps, it is conceivable that more bonding information could be obtained and thus the present work was undertaken.

### Experimental

A multipole atomic model for this compound with the valence density represented as a spherical harmonic series was refined based on the 105 K diffraction data (Wang & Liao, 1989), where 29 759 reflections were measured and 6861 unique reflections resulted after averaging of the equivalents, of which 5998 were considered to be observed and were used in the multipole refinements. According to the diffraction data at room temperature (Karle, Estlin & Britts, 1967; Wang, Liao & Ueng, 1986) and low temperature (Wang & Liao, 1989), there is no  $C_2$  symmetry in the molecule comparable with that in tetramethylthiuram disulfide (Wang, Liao & Ueng, 1986). However, the two halves of the molecule are chemically equivalent and the experimental deformation density of the two halves is essentially the same as mentioned earlier (Wang & Liao, 1989). Thus, the structure can be regarded as having a pseudo two-fold molecular symmetry at the midpoint of the S—S

bond (S2 and S3). In order to improve the accuracy and reduce the total number of parameters, a  $C_2$  axis was imposed on the molecule *via* the multipole terms for the corresponding atom pairs, *e.g.* S1/S4, S2/S3, N1/N2, C5/C6, *etc.* Spherical harmonic expansion terms (octapole<sup>+</sup> in Table 2) up to hexadecapoles were included for S atoms, up to octapoles for C and N atoms, and up to dipoles for H atoms. Multipole populations for the H atoms at methylene (C2, C3, C7 and C9) and at methyl (C1, C4, C8 and C10) carbon atoms, were constrained to be equal, *i.e.* H22 was constrained to H21, and H12 and H13 were constrained to H11, during the least-squares refinement. Multipole refinements were carried out with the *MOLLY* program (Hansen & Coppens, 1978). The core and valence scattering factors of all atoms were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV). He and Ne core electrons were used for C, N and S respectively. The valence electron configurations of S, C and N were  $s^2p^4$ ,  $s^2p^2$  and  $s^2p^3$  respectively, the parameters of radial functions according to the forementioned equation were as follows.  $n_l$  of S atom:  $n_0 = n_1 = n_2 = n_3 = n_4 = 4$ ;  $n_l$  of N atom:  $n_0 = n_1 = n_2 = 2$ ,  $n_3 = 3$ ,  $n_4 = 4$ ;  $n_l$  of C atom:  $n_0 = n_1 = n_2 = 2$ ,  $n_3 = 3$ ,  $n_4 = 4$ ;  $n_l$  of H atom:  $n_0 = 0$ ,  $n_1 = 1$ ;  $\zeta$  values of S, N, C and H were 3.95, 3.841, 3.176 and 2.0 respectively.

The deformation density maps were produced by subtracting the spherical atomic density from the sum of the atomic densities evaluated from the multipole expansion (octapole<sup>+</sup>). The dynamic deformation density evaluated is the density calculated including the nuclear vibration motion with Fourier coefficients up to the experimental data resolution (0.83 Å<sup>-1</sup>). The static deformation density evaluated is that which does not include the nuclear vibration and is based on Fourier coefficients up to the limiting sphere of Mo  $K\alpha$  radiation (1.41 Å<sup>-1</sup>, a total of 34 337 reflections). All calculations were carried out on a MicroVAX III computer.

An EHMO calculation for this molecule using the basis set given earlier (Gleiter & Hoffmann, 1968) was performed with the *ICON* program (Howell, Rossi, Wallace, Haraki & Hoffmann, 1977). The  $d$  polarization of the S atom was included in the analysis. The MO calculation was based on the coordinates from the diffraction data at 105 K (Wang & Liao, 1989). The theoretical deformation density was computed by subtracting the sum of spherical atomic densities (*i.e.*  $s^2p_x^{2/3}p_y^{2/3}p_z^{2/3}$  for C,  $s^2p_x^1p_y^1p_z^1$  for N,  $s^2p_x^{4/3}p_y^{4/3}p_z^{4/3}$  for S) from the total electron density calculated from the occupied molecular orbitals.

The *MOPLLOT* program (Lichtenberger & Fenske, 1975) was used for the density calculation, and contour plotting was carried out with a locally developed routine (Tsai, 1982).

## Results

Atomic parameters for non-H atoms from the multipole expansion refinement are given in Table 1. The full-matrix least-squares refinements were based on 5998 unique reflections and an extinction correction was applied. The extinction coefficient was  $0.297 \times 10^{-4}$ . The choice of local Cartesian axes for the multipole terms is shown in Fig. 1. Net atomic charges based on the multipole refinement up to monopole terms and on theoretical calculations are included in the figure. From the EHMO calculation, the charge on the H atoms of the methyl group and the charge on the H atoms of the methylene group are the average of all the methyl H atoms and of all the methylene H atoms respectively. The agreement indices at various stages of the multipole expansion are indicated in Table 2. The dynamic multipole deformation electron density distribution for the N—C=S plane shown in Fig. 2(a), represents the chemically unique half of the molecule. The deformation density around two sulfur atoms, S1 and S2, is shown in Figs. 2(b) and 2(c) with the planes perpendicular to Fig. 2(a) and normal to the C5—S1 vector and at the bisection of  $\angle C5-S2-S3$  respectively. The corresponding static deformation density maps are given in Fig. 3. The calculated density maps based on EHMO are given in Fig. 4. All the coefficients of multipole terms have been deposited.\*

## Discussion

There are positive density accumulations along the C—N, C—S and S—S bonds. Similar to the experimental deformation density results (Fig. 2b in Wang & Liao, 1989), the shorter C—N bond gives greater density accumulation at the midpoint of the bond than the longer one does. It is apparent that the lone-pair electron densities of the bridged (S2) and terminal (S1) sulfur atoms are located at the apex of the tetrahedron and trigonal bipyramid extending from the plane of N—C=S (Figs. 3 and 4 in Wang & Liao, 1989). The deformation densities along the bonds derived from the multipole model are much more pronounced than the experimental ones, but those of lone-pair regions are not so, although the features in both maps are quite similar. The prominence of the features in the multipole map might result from the fact that the structure factors  $F(h,k,l)$  are calculated based on a model, which serves as a

\* Lists of anisotropic temperature factors of non-H atoms, atomic parameters of H atoms, complete multipole coefficients of all atoms and structure factors after multipole refinement have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54900 (26 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Fractional atomic coordinates and  $B_{eq}$  values ( $\text{\AA}^2$ )

E.s.d.'s refer to the last digit printed.

$$B_{eq} = (8\pi^2/3) \sum_i \sum_j U_{ij} a_i^* a_j^* a_i a_j$$

	x	y	z	$B_{eq}$
S1	0.33898 (2)	0.32932 (1)	0.21373 (3)	1.519 (8)
S2	0.17112 (2)	0.45456 (1)	0.04102 (1)	1.119 (6)
S3	0.32819 (2)	0.51773 (1)	0.07938 (1)	1.111 (6)
S4	0.16513 (2)	0.57668 (1)	0.34449 (3)	1.583 (8)
N1	0.10016 (9)	0.30733 (6)	0.14728 (11)	1.06 (3)
N2	0.40213 (9)	0.61399 (6)	0.31758 (12)	1.17 (3)
C1	0.13509 (9)	0.15661 (6)	0.09321 (13)	1.47 (3)
C2	0.10602 (9)	0.22237 (6)	0.21609 (12)	1.23 (3)
C3	-0.02310 (8)	0.33558 (6)	0.09312 (12)	1.14 (3)
C4	-0.09151 (9)	0.37729 (6)	0.22580 (12)	1.45 (3)
C5	0.20037 (9)	0.35533 (6)	0.14237 (11)	1.02 (3)
C6	0.30153 (9)	0.57457 (6)	0.26267 (11)	1.04 (3)
C7	0.52404 (8)	0.60511 (6)	0.24810 (12)	1.24 (3)
C8	0.59311 (9)	0.53036 (6)	0.31815 (12)	1.51 (3)
C9	0.39797 (9)	0.66501 (7)	0.46314 (13)	1.53 (3)
C10	0.35468 (9)	0.75359 (7)	0.42814 (14)	1.94 (4)

Table 2. Least-squares results of multipole refinement (based on F)

$R_1 = \sum |F_o - kF_c| / \sum F_o$ ;  $R_{1w} = (\sum w|F_o - kF_c|^2 / \sum wF_o^2)^{1/2}$ ;  $R_2 = \sum |F_o^2 - kF_c^2| / \sum F_o^2$ ;  $R_{2w} = (\sum w|F_o^2 - kF_c^2|^2 / \sum wF_o^4)^{1/2}$ ;  $S = [\sum w|F_o - kF_c|^2 / (\text{NO} - \text{NV})]^{1/2}$ , NO = number of reflections, NV = number of variables.

	NV	$R_1$	$R_2$	$R_{1w}$	$R_{2w}$	S
Monopole	159	0.0286	0.0365	0.0206	0.0311	4.7955
Octapole	285	0.0213	0.0271	0.0145	0.0251	3.4097
Octapole* *	303	0.0207	0.0261	0.0141	0.0245	3.3267
Hexadecapole	357	0.0206	0.0258	0.0137	0.0237	3.2394

\* Up to hexadecapole terms for the S atoms only.

filter to filter out the unavoidable experimental errors from the direct measurement. In both maps, there is very little density accumulation along the S—S bond. However, there is clearly some positive electron density at about 0.9 Å from the bridged S nucleus in Fig.

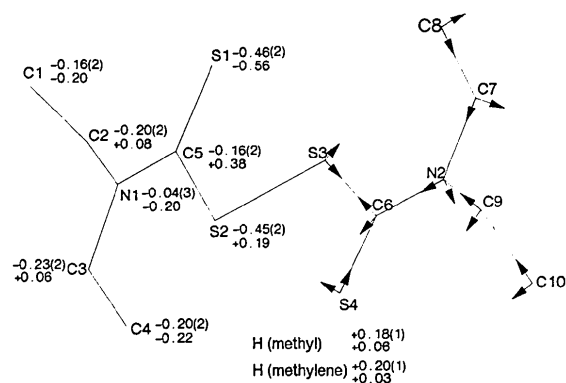
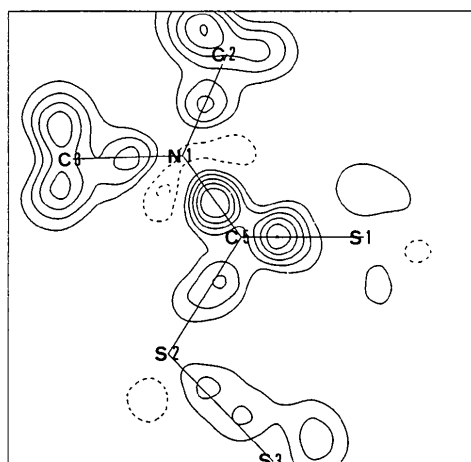
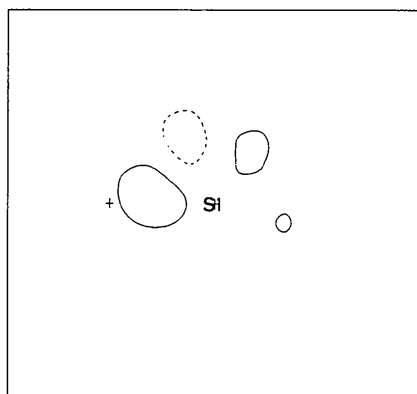


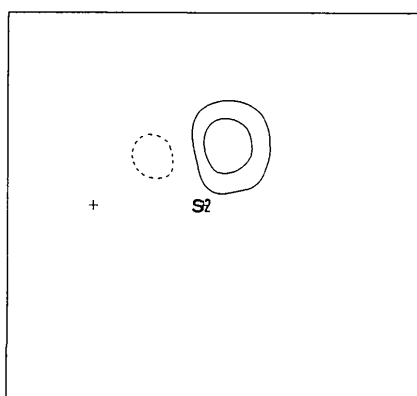
Fig. 1. Local Cartesian coordinates in the multipole model and the net atomic charge of tetraethylthiuram disulfide. The value given above is from the multipole model and the value below is for the EHMO calculation. All the arrows are the direction of x and y with x along the bonds.



(a)



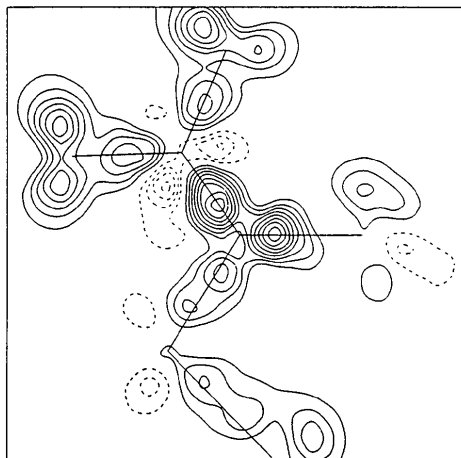
(b)



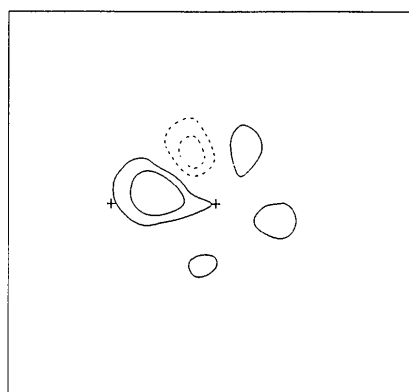
(c)

Fig. 2. Dynamic model deformation density maps. Solid line for positive contour, dotted for negative; contour interval is  $0.1 \text{ e } \text{\AA}^{-3}$ ; standard error of the map in the general position is  $0.03 \text{ e } \text{\AA}^{-3}$ . (a) N—C=S plane. (b) Plane perpendicular to (a) and normal to C5—S1 vector; the '+' is the projection of N1, and is  $2.437 \text{ \AA}$  in front of the plane shown. (c) Plane perpendicular to (a) and at the bisection of  $\angle \text{C5—S2—S3}$ ; the '+' is the projection of C5, and is  $1.427 \text{ \AA}$  in front of the plane shown.

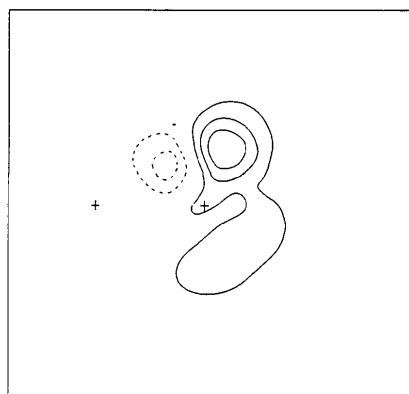
2(c) (and Fig. 4 in Wang & Liao, 1989). The features in the static and dynamic deformation density distributions are quite similar, but the densities are much larger in the static maps. These static density maps can be compared with those calculated theoretically. On refining the multipole model, the thermal param-



(a)



(b)



(c)

Fig. 3. Static model deformation density map. (a), (b) and (c) are defined as in Fig. 2; contour as in Fig. 2.

eters of the S atoms are reduced by 4%, whereas those of C and N atoms are increased by 2% or less. Thus, the multipole parameters are highly correlated with the thermal parameters for this structure. Further lower temperature work may resolve such

problems (Fabius, Cohen-Addad, Larsen, Lehmann & Becker, 1989).

The deformation densities obtained by EHMO calculations (Fig. 4) are qualitatively in agreement with those from the multipole model shown in Fig. 3, but with less positive densities along the bonds. However, there are much stronger lone-pair electron densities predominantly in the  $\pi$  directions near the S atoms. The lower density along the bond is probably due to the fact that only one electron's properties are taken into account in the EHMO method. The big difference near the nuclei between the experimental and theoretical maps is perhaps due to the difference in nuclear thermal vibration. Even in static maps, it is conceivable that the thermal motion still affects the density map. A lack of density accumulation along the C—S and S—S bonds has also been found elsewhere (Wang, Yeh, Wu, Pai, Lee & Lin, 1991; Wang, Wu & Cheng, 1990; Fabius, Cohen-Addad, Larsen, Lehmann & Becker, 1989). The lone-pair regions around S atoms are certainly more prominently represented in the theoretically calculated maps. When comparing the experimental (multipole static) and theoretical density maps, one also sees the difference between an isolated molecule and one in the solid state.

As indicated by Wang, Liao & Ueng (1986), the structure of the title compound can be described as two planar  $-\text{S}-(\text{CS})-\text{N}(\text{C})_4$  moieties connected by an S—S single bond. The planar monomer  $(\text{C})_4\text{NCS}_2^-$  anion can serve as a bidentate ligand with both S atoms as the electron donating site, *i.e.* the charge will be roughly equal for both S atoms. Thus the two C—S distances of such a complex will be between the single C—S bond lengths [1.820 and 1.825 (2) Å] and the double C=S bond length [1.643 (2) Å] of the title compound (Wang, Liao & Ueng, 1986). For example, in some metal complexes, (Huang, Zhuang, Yang & Lu, 1986; Pan, Halbert, Hutchings & Stiefel, 1985), it has been found that the C—S distances are 1.716–1.752 (3) Å. Furthermore,  $-\text{C}(2)_2\text{M}$  are nearly planar, and some degree of  $\pi$  delocalization is believed to exist in such a planar molecule.

Net atomic charges can be obtained both from multipole refinements and from the theoretical calculations. However, the two results are not quite comparable. It is generally accepted that the terminal S atom is more electron rich than for bridged S atoms, and this is supported by the EHMO calculations ( $-0.56$  versus  $+0.19$  in Fig. 1). However this is not the case for the net atomic charge from the multipole refinement ( $-0.46$  versus  $-0.45$ ), which seems to imply that it is close to the metal complex case mentioned above. The net atomic charges from EHMO are in better agreement with the results from the refinements including up to monopole terms than

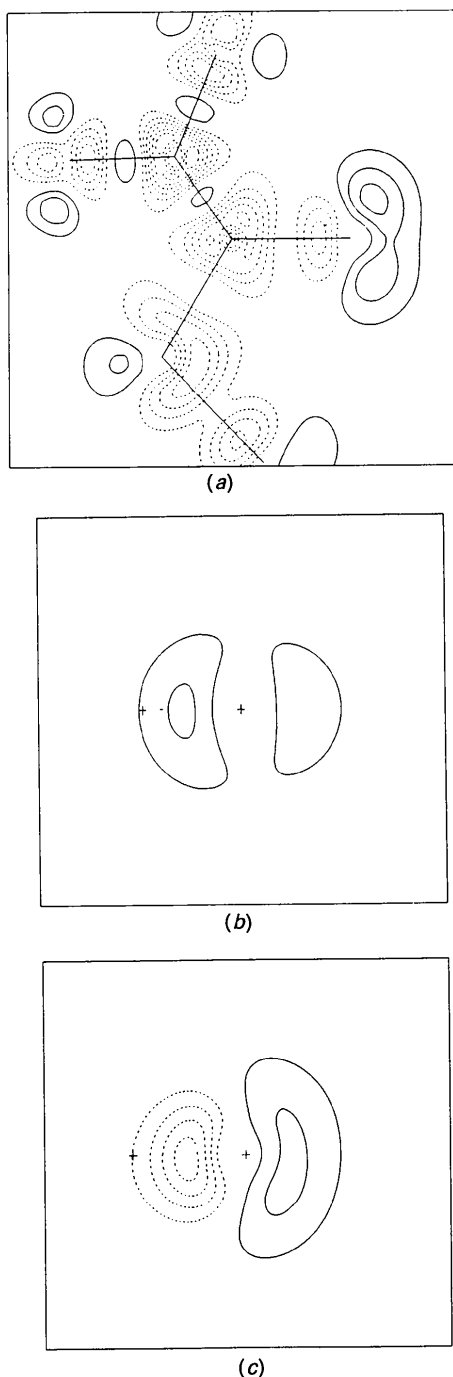


Fig. 4. Theoretical deformation density map based on EHMO calculation. (a), (b) and (c) are defined as in Fig. 2; contours as in Fig. 2.

those from the refinements including up to hexadecapole terms [e.g.  $-0.56$  (EHMO),  $-0.46$  (monopole) and  $-0.2$  (octapole<sup>+</sup>) for S1]. This may be the result of correlations among the coefficients of multipole terms,  $P_{lm}$ , and the thermal parameters,  $U_{ij}$ .

Thanks are due to the National Science Council of ROC for financial support.

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*Acta Cryst.* (1992). **B48**, 324–329

## Comparison of Twists in Isosteric Propellers: X-ray Structures of Tris(2,6-dimethoxyphenyl)borane, Tris(2,6-dimethoxyphenyl)methyl Cation and Tris(2,6-dimethoxyphenyl)methyl Radical

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(Received 19 March 1991; accepted 17 December 1991)

#### Abstract

The X-ray structures of three per-*o*-methoxytriphenyl-*X* molecules were determined by direct methods. Tris(2,6-dimethoxyphenyl)borane (1),  $C_{24}H_{27}BO_6$ ,  $M_r = 422.3$ , monoclinic,  $C2/c$ ,  $a = 11.076$  (5),  $b = 20.839$  (8),  $c = 9.944$  (4) Å,  $\beta = 98.40$  (3)°,  $V = 2271$  (1) Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 1.24$  g cm<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.71073$  Å,  $\mu = 0.8$  cm<sup>-1</sup>,  $F(000) = 896$ ,  $T = 295$  K. Refinement based on 926 unique observed reflections and 170 parameters gave a final  $R(F_o) = 0.045$ . The tetrafluoroborate salt of the isoelectronic tris(2,6-dimethoxyphenyl)methyl cation (2),  $C_{25}H_{27}O_6^+ \cdot BF_4^-$ ,  $M_r = 510.3$ , triclinic,  $P\bar{1}$ ,  $a = 7.214$  (5),  $b = 12.931$  (4),  $c = 13.633$  (3) Å,  $\alpha = 83.13$  (2),  $\beta = 77.70$  (3),  $\gamma = 80.56$  (4)°,  $V =$

1221 (1) Å<sup>3</sup>,  $Z = 2$ ,  $D_x = 1.39$  g cm<sup>-3</sup>,  $\lambda(\text{Cu } K\alpha) = 1.5418$  Å,  $\mu = 9.7$  cm<sup>-1</sup>,  $F(000) = 532$ ,  $T = 110$  K. Refinement based on 2393 unique observed reflections and 325 parameters gave a final  $R(F_o) = 0.056$ . Tris(2,6-dimethoxyphenyl)methyl radical (3),  $C_{25}H_{27}O_6$ ,  $M_r = 423.5$ , monoclinic,  $P2/n$ ,  $a = 10.405$  (1),  $b = 9.429$  (2),  $c = 11.767$  (2) Å,  $\beta = 102.120$  (9)°,  $V = 1128.7$  (6) Å<sup>3</sup>,  $Z = 2$ ,  $D_x = 1.25$  g cm<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.71073$  Å,  $\mu = 0.8$  cm<sup>-1</sup>,  $F(000) = 450$ ,  $T = 295$  K. Refinement based on 1189 unique observed reflections and 142 parameters gave a final  $R(F_o) = 0.059$ . The borane (1) adopts an approximate  $D_3$  conformation in the lattice at a site with crystallographic  $C_2$  symmetry and aryl twist angles of 62.8 (2) and 64.18 (2)° for the special and general rings. The cation (2) adopts a general posi-