

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

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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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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) Å³, $Z = 4$, $D_x = 1.24$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.71073$ Å, $\mu = 0.8$ cm⁻¹, $F(000) = 896$, $T = 295$ 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) Å³, $Z = 2$, $D_x = 1.39$ g cm⁻³, $\lambda(\text{Cu } K\alpha) = 1.5418$ Å, $\mu = 9.7$ cm⁻¹, $F(000) = 532$, $T = 110$ 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) Å³, $Z = 2$, $D_x = 1.25$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.71073$ Å, $\mu = 0.8$ cm⁻¹, $F(000) = 450$, $T = 295$ 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-

Table 1. Crystal structure determination and refinement data for tris(2,6-dimethoxyphenyl)borane (1), tris(2,6-dimethoxyphenyl)methyl cation (2) and tris(2,6-dimethoxyphenyl)methyl radical (3)

| | (1) | (2) | (3) |
|------------------------------------|--|--|--|
| Formula | $C_{24}H_{27}BO_6$ | $C_{24}H_{27}O_6^+ \cdot BF_4^-$ | $C_{24}H_{27}O_6$ |
| M_r | 422.3 | 510.3 | 423.5 |
| Space group | $C2/c$ | $P1$ | $P2/n$ |
| Z | 4 | 2 | 2 |
| Temperature (K) | 295 | 110 | 295 |
| Cell dimensions | | | |
| a (Å) | 11.076 (5) | 7.214 (5) | 10.405 (1) |
| b (Å) | 20.839 (8) | 12.931 (4) | 9.429 (2) |
| c (Å) | 9.944 (4) | 13.633 (3) | 11.767 (2) |
| α (°) | 90 | 83.13 (2) | 90 |
| β (°) | 98.40 (3) | 77.70 (3) | 102.120 (9) |
| γ (°) | 90 | 80.56 (4) | 90 |
| μ (cm ⁻¹) | 0.8 (Mo $K\alpha$) | 9.7 (Cu $K\alpha$) | 0.8 (Mo $K\alpha$) |
| D_x (g cm ⁻³) | 1.24 | 1.39 | 1.25 |
| Experimental data | | | |
| Crystal dimensions (mm) | 0.2 × 0.4 × 0.4 | 0.3 × 0.3 × 1.3 | 0.25 × 0.3 × 0.4 |
| Reflections measured | 2183 | 2517 | 2748 |
| Unique observed data | 926 $F_o^2 > 3\sigma(F_o^2)$ | 2386 $I > 3\sigma(I)$ | 1189 $F_o > 3\sigma(F_o)$ |
| Range of h,k,l | $0 \leq h \leq 13$ $0 \leq k \leq 24$ $-11 \leq l \leq 11$ | $-7 \leq h \leq 0$ $-12 \leq k \leq 12$ $-13 \leq l \leq 13$ | $-13 \leq h \leq 13$ $0 \leq k \leq 12$ $0 \leq l \leq 15$ |
| $2\theta_{max}$ (°) | 50 | 100 | 55 |
| $R(F_o)$ | 0.045 | 0.056 | 0.059 |
| $wR(F_o)$ | 0.041 | 0.079 | 0.073 |
| Weighting scheme | 1 | $\sigma^{-2}(F_o)$ | $\sigma^{-2}(F_o)$ |
| S | 0.70 | 3.70 | 1.53 |
| Max. LS shift/e.s.d. | 0.07 | 0.0 | 0.11 |
| Number of parameters | 170 | 325 | 142 |
| Residual peak (e Å ⁻³) | 0.28 | 0.4 | 0.4 |
| Function minimized | $\sum w(F_o - F_c)^2$ | $\sum w(F_o - F_c)^2$ | $\sum w(F_o - F_c)^2$ |

tion in the lattice with approximate C_2 symmetry. The aryl twist angles are 32.6 (2), 46.1 (2) and 48.9 (2)°. The free radical (3) adopts a conformation that deviates markedly from the expected ground-state structure; the special ring on a crystallographic C_2 axis is twisted out of the plane of coordination by only 12.3 (5)° while the general rings are twisted by 61.0 (1)°.

Introduction

Single-crystal structure determinations of tris(2,6-dimethoxyphenyl)borane (1), tris(2,6-dimethoxyphenyl)methyl cation (2) and tris(2,6-dimethoxyphenyl)methyl radical (3) were undertaken to characterize the shape of the nucleophilic pocket formed by a tripod of methoxy groups that shield the central atom in D_3 and approximate D_3 conformations. This series of X-ray structures allowed direct comparisons of the isoelectronic species (1) and (2), the isosteric neutral species (1) and (3), and the similarly substituted triarylmethyl cation (2) and triarylmethyl radical (3).

Experimental

Tris(2,6-dimethoxyphenyl)borane (1) was prepared from 2,6-dimethoxyphenyllithium and boron trifluoride etherate. Needles were obtained by slow

evaporation of a methylene chloride solution at room temperature. Tris(2,6-dimethoxyphenyl)methyl (3) is an air-stable free radical that was prepared according to known procedures (Sabacky, Johnson, Smith, Gutowsky & Martin, 1967). Brick-red monoclinic prisms were obtained by evaporation of an ether solution in air. Crystals of the tetrafluoroborate salt of the tris(2,6-dimethoxyphenyl)methyl cation (2) were first prepared by oxidizing (3) in the presence of lithium tetrafluoroborate (Kahr & Jackson, 1985). They were later obtained in a more straightforward manner by treating tris(2,6-dimethoxyphenyl)methanol (Martin & Smith, 1964) in 10% H_2SO_4 with a 48% solution of HBf_4 . The resulting metallic green precipitate was filtered and recrystallized from acetone to give thin plates.

The crystallographic data, experimental conditions, and refinement data are summarized in Table 1.* In each case the cell constants were initially determined by fitting 25 low-angle reflections [$(1) 7.5 < \theta < 12.5^\circ$, $(2) 10 < \theta < 21^\circ$, $(3) 7 < \theta < 12^\circ$]. The intensities of (1) were measured at room temperature on a Nicolet P3F diffractometer using graphite-

* Lists of structure factors, anisotropic thermal parameters, bond lengths and angles, and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54848 (46 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

monochromated Cu $K\alpha$ radiation and an ω - 2θ scan. Absorption corrections were applied using the program *DIFABS* (Walker & Stuart, 1983). Equivalent reflections were averaged to give $R_{\text{int}}(F_o) = 0.024$. A secondary-extinction coefficient was applied. The final refined coefficient was 6.0×10^{-7} in absolute units (Zachariasen, 1963).

The intensities of (2) were measured on an Enraf-Nonius CAD-4 diffractometer at 110 K using graphite-monochromated Mo $K\alpha$ radiation and an ω - 2θ scan. Seven reflections that were strongly affected by extinction were excluded from the final refinement and difference map. No absorption corrections were applied. Similarly, the intensities of (3) were measured on an Enraf-Nonius CAD-4 diffractometer at room temperature using graphite-monochromated Mo $K\alpha$ radiation and an ω - 2θ scan. No absorption corrections were applied. The repeated measurements of three standard reflections for (1), (2) and (3) revealed no appreciable decay during the course any of the data collections.

The structures of (1) and (3) were solved by direct methods employed in *SHELXS86* (Sheldrick, 1986), while the structure of (2) was solved with the direct-methods program *MULTAN82* (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1982). Standard scattering factors were employed (Cromer & Waber, 1974). All non-H atoms were refined anisotropically. H atoms were included at calculated idealized positions except for the phenyl hydrogens of (1) which were located in difference maps in the later stages of the Fourier synthesis, and whose positions were refined. In each case computations were performed on a VAX computer using *SDP/VAX* software (Frenz, 1978).

Discussion

The solid-state conformations of symmetrically substituted Ar_3X compounds (where $\text{X} = \text{B}, \text{C}$ or N) adopt D_3 or approximate D_3 conformations where all the rings are similarly twisted out of the coordination plane of the central atom. Compound (1) conforms to this structural pattern in the crystalline state. The borane (1) lies along the twofold axis and the mean planes of the special and general aryl rings adopt angles of 62.8 (2) and 64.18 (2) $^\circ$ with respect to the coordination plane of the boron atom. The cation (2), which is isoelectronic with the borane (1), deviates from D_3 symmetry in the lattice but it can still be described as a propeller with aryl twist angles of 32.6 (2), 46.1 (2) and 48.9 (2) $^\circ$. These values are similarly measured as the angles between mean aryl ring planes and the plane of the atoms to which the central carbon is bonded. Since the twist angles are the parameters that most affect the shape of the molecule, cation (2) can be said to adopt an approxi-

mate C_2 conformation on a general position in the lattice. Nevertheless, the disparity between the ring torsion angles is not so great that (2) cannot be described as having a propeller conformation; it is effectively planar in that the central atom C1 rises only 0.08 \AA out of the plane of the atoms to which it is bonded (C11, C21, C31). Views of (1) and (2) normal to their least-squares planes, along with the labeling schemes, are presented in Fig. 1 while the atomic parameters are listed in Tables 2 and 3, respectively.

As a consequence of the propeller conformations of (1) and (2) the methoxy groups are arranged in such a way that they form a pair of nucleophilic oxygen pockets situated on either side of the mean molecular plane with the lone-electron pairs projecting toward the centers of small cavities. The cofacial oxygen-oxygen distances in (1) range from 3.17 to 4.27 \AA while the corresponding distances for (2) range from 3.62 to 4.27 \AA . Studies of the complexation of (1) and (3) with small cations and the

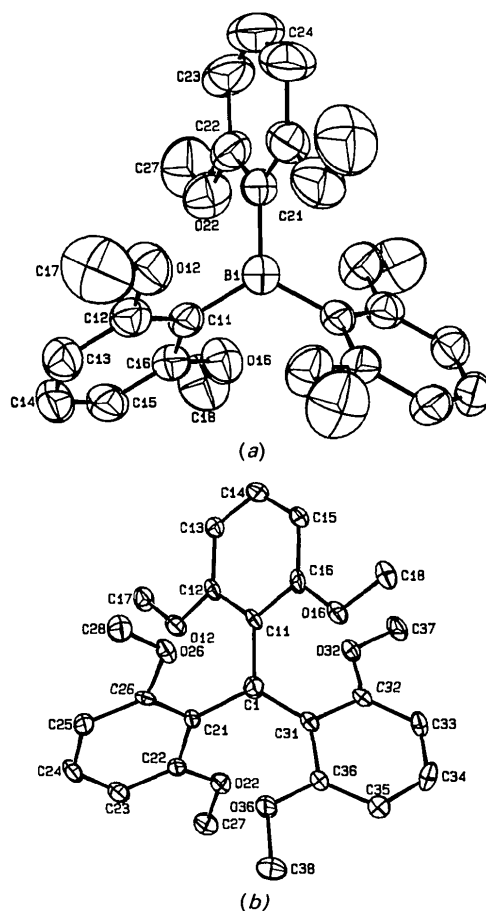


Fig. 1. View normal to the least-squares planes of (a) (1) and (b) (2) showing the labeling scheme. H atoms have been deleted for clarity. Thermal ellipsoids are 50% probability.

Table 2. Atomic positional and isotropic thermal parameters for tris(2,6-dimethoxyphenyl)borane (1)

| | x | y | z | B (Å ²) |
|-----|-------------|------------|-------------|---------------------|
| O12 | -0.1768 (2) | 0.1640 (1) | 0.4236 (3) | 5.76 (7) |
| O16 | -0.0679 (2) | 0.0783 (1) | 0.0287 (3) | 5.46 (6) |
| O22 | -0.0872 (3) | 0.2303 (1) | 0.0245 (3) | 6.24 (7) |
| C11 | -0.1238 (3) | 0.1191 (2) | 0.2279 (3) | 3.35 (7) |
| C12 | -0.2089 (3) | 0.1235 (2) | 0.3162 (4) | 4.07 (8) |
| C13 | -0.3181 (3) | 0.0887 (2) | 0.2971 (4) | 5.00 (9) |
| C14 | -0.3414 (3) | 0.0501 (2) | 0.1859 (4) | 5.3 (1) |
| C15 | -0.2625 (3) | 0.0445 (2) | 0.0930 (4) | 4.84 (9) |
| C16 | -0.1529 (3) | 0.0796 (2) | 0.1157 (4) | 4.04 (8) |
| C17 | -0.2448 (5) | 0.1633 (3) | 0.5329 (5) | 9.5 (2) |
| C18 | -0.1025 (5) | 0.0549 (3) | -0.1045 (4) | 8.1 (1) |
| C21 | 0.000 | 0.2324 (2) | 0.250 | 3.8 (1) |
| C22 | -0.0450 (4) | 0.2670 (2) | 0.1341 (4) | 4.98 (9) |
| C23 | -0.0467 (4) | 0.3343 (2) | 0.1343 (5) | 7.1 (1) |
| C24 | 0.000 | 0.3652 (3) | 0.250 | 7.9 (2) |
| C27 | -0.1235 (5) | 0.2601 (3) | -0.1040 (5) | 9.0 (2) |
| B1 | 0.000 | 0.1573 (3) | 0.250 | 3.3 (1) |

Table 3. Atomic positional and isotropic thermal parameters for tris(2,6-dimethoxyphenyl)methyl cation (2)

| | x | y | z | B (Å ²) |
|-----|------------|------------|------------|---------------------|
| C1 | 0.8591 (4) | 0.7456 (2) | 0.7626 (2) | 1.63 (6) |
| O12 | 1.0832 (3) | 0.5854 (1) | 0.8561 (1) | 2.10 (4) |
| O16 | 0.5769 (2) | 0.6873 (1) | 0.6799 (1) | 2.08 (4) |
| O22 | 1.1496 (2) | 0.8571 (1) | 0.7706 (1) | 2.10 (4) |
| O26 | 0.5931 (3) | 0.7186 (1) | 0.9383 (1) | 2.15 (4) |
| O32 | 1.0211 (3) | 0.6716 (1) | 0.5759 (1) | 2.09 (4) |
| O36 | 0.7445 (3) | 0.9616 (1) | 0.7615 (1) | 2.38 (4) |
| C11 | 0.8308 (4) | 0.6359 (2) | 0.7670 (2) | 1.60 (6) |
| C12 | 0.9479 (4) | 0.5547 (2) | 0.8146 (2) | 1.71 (6) |
| C13 | 0.9275 (4) | 0.4498 (2) | 0.8140 (2) | 1.90 (6) |
| C14 | 0.7915 (4) | 0.4255 (2) | 0.7661 (2) | 2.06 (6) |
| C15 | 0.6695 (4) | 0.5030 (2) | 0.7206 (2) | 1.80 (6) |
| C16 | 0.6912 (4) | 0.6067 (2) | 0.7202 (2) | 1.72 (6) |
| C17 | 1.2214 (4) | 0.5041 (2) | 0.8910 (2) | 2.20 (6) |
| C18 | 0.4320 (4) | 0.6626 (2) | 0.6317 (2) | 2.42 (6) |
| C21 | 0.8765 (4) | 0.7837 (2) | 0.8565 (2) | 1.55 (6) |
| C22 | 1.0300 (4) | 0.8388 (2) | 0.8600 (2) | 1.80 (6) |
| C23 | 1.0541 (4) | 0.8677 (2) | 0.9506 (2) | 2.09 (6) |
| C24 | 0.9256 (4) | 0.8419 (2) | 1.0385 (2) | 2.25 (6) |
| C25 | 0.7716 (4) | 0.7910 (2) | 1.0382 (2) | 1.91 (6) |
| C26 | 0.7473 (4) | 0.7629 (2) | 0.9472 (2) | 1.62 (6) |
| C27 | 1.3168 (4) | 0.9035 (2) | 0.7711 (2) | 2.53 (6) |
| C28 | 0.4488 (4) | 0.7028 (2) | 1.0258 (2) | 2.24 (6) |
| C31 | 0.8656 (4) | 0.8113 (2) | 0.6719 (2) | 1.60 (6) |
| C32 | 0.9267 (4) | 0.7698 (2) | 0.5746 (2) | 1.70 (6) |
| C33 | 0.8989 (4) | 0.8302 (2) | 0.4874 (2) | 2.23 (6) |
| C34 | 0.8091 (4) | 0.9329 (2) | 0.4941 (2) | 2.56 (6) |
| C35 | 0.7575 (4) | 0.9808 (2) | 0.5838 (2) | 2.15 (6) |
| C36 | 0.7901 (4) | 0.9222 (2) | 0.6709 (2) | 1.74 (6) |
| C37 | 1.1011 (4) | 0.6265 (2) | 0.4816 (2) | 2.33 (6) |
| C38 | 0.6686 (5) | 1.0712 (2) | 0.7669 (2) | 2.87 (7) |
| F1 | 0.4731 (2) | 0.2961 (1) | 0.7397 (1) | 2.49 (3) |
| F2 | 0.4924 (2) | 0.2215 (1) | 0.5947 (1) | 2.80 (4) |
| F3 | 0.2166 (2) | 0.2304 (1) | 0.7131 (1) | 3.25 (4) |
| F4 | 0.3067 (3) | 0.3797 (1) | 0.6215 (1) | 3.46 (4) |
| B1 | 0.3713 (5) | 0.2822 (2) | 0.6658 (2) | 1.97 (7) |

properties of the resulting aggregates will be reported elsewhere. The persistence of the nucleophilic oxygen pocket in (2) can be viewed in the space-filling image in Fig. 2.

The conformation of the free radical (3) stands in marked contrast to (1) and (2) and all other triarylmethyl free-radical X-ray structures. Rather than

Table 4. Atomic positional and isotropic thermal parameters for tris(2,6-dimethoxyphenyl)methyl radical (3)

| | x | y | z | B (Å ²) |
|-----|-------------|-------------|------------|---------------------|
| O1 | 0.0794 (3) | -0.0518 (3) | 0.3549 (2) | 4.29 (6) |
| O2 | 0.2947 (3) | 0.2839 (3) | 0.4378 (2) | 4.49 (7) |
| O3 | -0.0081 (2) | 0.0940 (3) | 0.1272 (2) | 4.20 (6) |
| C1 | ↓ | 0.1074 (6) | ↓ | 2.6 (1) |
| C2 | ↓ | -0.0431 (6) | ↓ | 2.7 (1) |
| C3 | 0.1603 (4) | -0.1258 (5) | 0.2996 (3) | 3.42 (8) |
| C4 | 0.1588 (5) | -0.2717 (5) | 0.2975 (4) | 4.8 (1) |
| C5 | ↓ | -0.3437 (8) | ↓ | 6.0 (2) |
| C6 | -0.0331 (5) | -0.1189 (7) | 0.3790 (6) | 7.7 (2) |
| C7 | 0.1433 (3) | 0.1955 (4) | 0.2785 (3) | 2.67 (7) |
| C8 | 0.1706 (3) | 0.2929 (4) | 0.3703 (3) | 3.07 (8) |
| C9 | 0.0767 (4) | 0.3854 (5) | 0.3935 (3) | 4.0 (1) |
| C10 | -0.0479 (4) | 0.3830 (5) | 0.3229 (4) | 4.4 (1) |
| C11 | -0.0800 (4) | 0.2871 (5) | 0.2330 (4) | 4.2 (1) |
| C12 | 0.0147 (3) | 0.1934 (5) | 0.2119 (3) | 3.09 (8) |
| C13 | 0.3359 (5) | 0.3823 (7) | 0.5281 (5) | 7.2 (1) |
| C14 | -0.1360 (5) | 0.0840 (7) | 0.0564 (5) | 7.4 (2) |

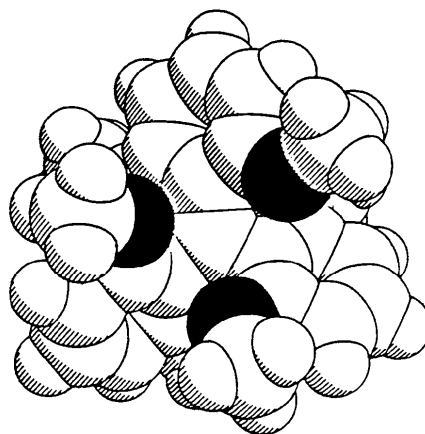


Fig. 2. Space-filling model of (2) viewed normal to the least-squares plane. The nucleophilic oxygen pocket persists even in the C₂ conformation. Filled atoms are oxygens.

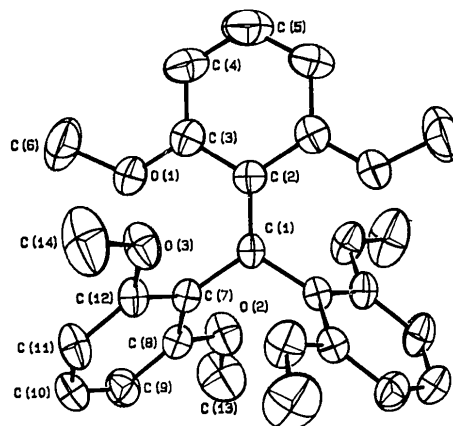


Fig. 3. View normal to the least-squares planes of (3) showing the labeling scheme. H atoms have been deleted for clarity. Thermal ellipsoids are 50% probability.

Table 5. Selected bond lengths (Å), bond angles (°) and torsion angles (°) for tris(2,6-dimethoxyphenyl)borane (1), tris(2,6-dimethoxyphenyl)methyl cation (2) and tris(2,6-dimethoxyphenyl)methyl radical (3)

| | (1) | (2) | (3) |
|-------------------------------|------------|--------------------------|-------------------------|
| $C_{ar}-X$ | | | |
| B1—C11 | 1.574 (4) | C1—C11 1.458 (4) | C1—C2 1.419 (6) |
| B1—C21 | 1.565 (7) | C1—C21 1.462 (4) | C1—C7 1.481 (4) |
| | | C1—C31 1.411 (3) | |
| $C_{ar}-X-C_{ar}$ | | | |
| C11—B1—C11 | 119.2 (2) | C11—C1—C21 116.8 (2) | C2—C1—C7 124.2 (4) |
| C11—B1—C21 | 120.4 (2) | C11—C1—C31 121.0 (2) | C7—C1—C7 111.7 (4) |
| | | C21—C1—C31 122.2 (2) | |
| $C_{ar}-X-C_{ipso}-C_{ortho}$ | | | |
| C21—B1—C11—C1 | -62.1 (1) | C11—C1—C21—C22 130.2 (3) | C7—C1—C2—C3 -12.9 (2) |
| C21—B1—C11—C16 | 116.94 (9) | C11—C1—C21—C26 -46.8 (2) | C2—C1—C7—C8 121.5 (3) |
| C11—B1—C11—C12 | 117.8 (2) | C11—C1—C31—C32 -27.1 (4) | C2—C1—C7—C12 -63.02 (4) |
| C11—B1—C11—C16 | -63.1 (2) | C11—C1—C31—C36 145.4 (3) | C7—C1—C7—C8 -58.5 (3) |
| C11—B1—C21—C22 | -64.6 (2) | C21—C1—C11—C12 -47.9 (2) | C7—C1—C7—C12 117.0 (3) |
| | | C21—C1—C11—C16 135.0 (3) | |
| | | C21—C1—C31—C32 154.1 (3) | |
| | | C21—C1—C31—C36 -33.4 (4) | |
| | | C31—C1—C11—C12 133.3 (3) | |
| | | C31—C1—C11—C16 -43.9 (4) | |
| | | C31—C1—C21—C22 -51.0 (4) | |
| | | C31—C1—C21—C26 132.0 (3) | |

the anticipated D_3 conformation the aryl rings are dissimilarly twisted; the ring on the crystallographic twofold axis is nearly in the plane of the central C atom [12.2 (2)°] while the general rings are twisted out of this plane by 61.0 (1)°. ESR hyperfine coupling constants in solution suggest a D_3 structure in which the aryl rings are twisted out-of-plane by 50° (Sabacky, Johnson, Smith, Gutowsky & Martin, 1967). The X-ray positional parameters for (3) are listed in Table 4 while Fig. 3 shows a view normal to the mean plane of the molecule based on this labeling scheme. Table 5 compares salient features of the molecular geometries common to (1), (2) and (3).

Variations in the conjugation of the respective aryl rings in (3) are reflected in the inequivalence of the $C_{methyl}-C_{aryl}$ bond lengths: 1.419 (6) Å for the special ring and 1.481 (4) Å for the general rings. Similarly, the unique $C_{aryl}-C_{methyl}-C_{aryl}$ angle is dramatically diminished to 111.7 (4)° while the adjacent valence angles fill out the circle at 124.2 (4)°.

Modest deviations from idealized D_3 conformations to C_2 or approximate C_2 conformations have been observed in the three previously determined triarylmethyl radical crystal structures. The ring twists in the C_2 structure tri-*p*-nitrophenylmethyl (Andersen & Klewe, 1967) are 30 and 40°, while corresponding twists in tris(3,5-di-*tert*-butylphenyl)methyl (Kahr, 1988) are 31.2 and 36.0°. Twist angles in the C_1 perchlorotriphenylmethyl structure (Veciana, Carilla, Miravittles & Molins, 1987) approximate a C_2 conformation at 46.3, 53.4 and 53.8°.

The lowest-energy pathway for the racemization of Ar_3X compounds is the two-ring flip mechanism

(Mislow, 1976). Increased racemization barriers are consistent with large *ortho* substituents; perchlorotriphenylmethyl does not racemize on the room temperature time scale (Ballester, Riera, Castaner, Badia & Monsó, 1971; Hayes, Nagamo, Blount & Mislow, 1980). It was therefore surprising to us to have found an aryl twist of 12° in (3), a per-*ortho*-substituted triarylmethyl.

The solid-state conformation of (3) represents a point well along the way toward the transition state of the two-ring flip process. Evidence for the two-ring flip racemization in triphenylphosphines was provided by sample-point distributions from structures in the Cambridge Structural Database (1989) (see Bye, Schweitzer & Dunitz, 1982). Force-field calculations suggest a racemization barrier of about 10 Kcal mol⁻¹ for (3) (Jackson & Jang, 1990).*

It was shown recently that the solid-state conformations of trimesitylborane and the trimesitylborane radical anion are virtually identical (Olmstead & Power, 1986). The conclusion of this comparative study was that the structural consequences of the addition of one electron into the LUMO of a compound of the type Ar_3X are trivial. While this conclusion is supported by a tendency toward D_3 symmetry in many reported structures of triarylboranes, triarylmethyls and triarylaminines, the gross differences in the conformations of (2) and (3), which also differ by only a single electron, caution that such a conclusion should not be drawn from a comparison of only two crystal structures.

* Obtained using the PCMODEL program (Gilbert & Gajewski, 1989).

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Neutron Diffraction and Calorimetric Studies of Methylammonium Iodide*

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Abstract

A powerful combination of calorimetric and high-resolution neutron powder-diffraction techniques has been used to study the phase transitions in deuterated methylammonium iodide. The neutron powder-diffraction measurements have confirmed the four-fold disorder of the deuterium atoms about the C_3 axis of the methylammonium ion in the tetragonal ($P4/nmm$) α' phase. The structure of the metastable δ phase was determined using a novel method of chemically constrained profile refinement. It was found to be orthorhombic ($Pbma$, $Z = 4$, $a = 7.1743$, $b = 7.0967$, $c = 8.8323$ Å) in which the deuterium

atoms were completely ordered in an anti-parallel manner along the b axis. Heat capacities of the α' and δ phases of CD_3ND_3I were measured in the temperature range 13–303 K. A continuous λ -type anomaly was found at the δ - α' phase transition which occurred at 164.0 K with an associated transition entropy of $8.8 \text{ J K}^{-1} \text{ mol}^{-1}$. The results are very similar to those of CH_3NH_3I measured previously, indicating that deuteration of the methylammonium ion does not affect the mechanism of the δ - α' phase transition of CD_3ND_3I .

1. Introduction

CH_3NH_3X ($X = \text{Cl, Br, I}$) compounds have many polymorphs related to the various types of orientational disorder of the methylammonium ($CH_3NH_3^+$) ion. In the high-temperature ϵ phase (observed only

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