

2).* The final difference density map gave $\Delta\rho = \pm 0.2 e \text{ \AA}^{-3}$.

Results and discussion

The electrostatic potential (Fig. 1) is shown for a molecule of benzamide which is removed from the crystal, but which retains the effects of its crystal environment. There is surprisingly good agreement between the electrostatic potential of the phenyl ring for this model (Fig. 1) and that of benzene itself (Stewart, 1991). There are no significant variations in potential around C(3) and C(5) which might account for the *meta*-directing properties of the molecule. The population parameters given in Table 2 show no indication of an increased density at these positions. The potential in the C(2) and C(6) region is similar, being only slightly contracted. The apparent minor differences between the electrostatic potential for benzene and that for benzamide are probably due to several factors. One is that the O—C(7)—C(1)—C(6) torsion angle of $-25.3(1)^\circ$ observed in the crystal structure precludes resonance between the phenyl ring and the substituent. Another is that hydrogen bonding minimizes the inductive effect. Other than hydrogen bonding, there are no significant intermolecular interactions less than 3.4 Å. A packing diagram is given in Fig. 2. A third factor could be that the

effects of the amido substituent are much weaker and might only be observable in the σ -complex itself. The deformation density (Fig. 5) for the non-H atoms in benzamide is similar to that observed in *para*-fluorobenzamide (Kubota & Ohba, 1992), which has an O—C(7)—C(1)—C(2) torsion angle of $-26.7(3)^\circ$.

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* A list of observed and calculated structure factors and electrostatic potential diagrams have been deposited with the IUCr (Reference: BK0008). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Structure of 1,3,5-Trichloro-2,4,6-trimethylbenzene at 150 and 297 K, Molecular Motion and Reorientation

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Abstract

$\text{C}_9\text{H}_3\text{Cl}_3$, triclinic $P\bar{1}$ with $Z=2$, $M_r=223.53$, crystal data at 150 K [297]: $a=7.646(3)$ [7.738(6)], $b=8.789(6)$ [8.842(4)], $c=8.827(3)$ Å [8.880(3)], $\alpha=59.78(4)$ [59.74(3)], $\beta=66.03(3)$ [66.51(5)], $\gamma=72.69(4)^\circ$ [73.06(4)], $V=465.1 \text{ \AA}^3$ [478.1], $D_x=1.593 \text{ g cm}^{-3}$ [1.553], $\text{Mo K}\alpha$, $\lambda=0.71073 \text{ \AA}$,

$\mu=9.278 \text{ cm}^{-1}$ [9.025], $F(000)=228$, $R=0.0349$ [0.0378], $wR=0.0472$ [0.0506] for 1222 [1074] reflections with $I \geq 3\sigma(I)$. The thermal motion of 1,3,5-trichloro-2,4,6-trimethylbenzene (or TCM) is rather high; no disorder can be detected in the range 150–297 K and X-rays provide information on H atoms. The quantum chemistry program AM1 gives a molecular conformation in reasonable accordance with

the experimental results. Using atom–atom interactions of Buckingham-type, we were able to calculate phonon frequencies in accordance with spectroscopic results. From the calculus of the variations of the crystalline potential energy when one molecule is rotated in its plane and from protonic magnetic resonance results, we can understand why, above 150 K, TCM molecules undergo fast $2\pi/3$ reorientations while keeping an ordered structure. Furthermore, we were able to explain why each of the three methyls in one molecule has a specific tunneling splitting.

1. Introduction

Structure of the hexasubstituted benzenes at 300 K and frequent occurrence of dynamical disorder

There is no need to present here a detailed review of all the studies on hexasubstituted benzenes (HSB), but it is necessary to present the main tendencies before discussing the TCM case. Already in his monograph 'Molecular Crystals and Molecules' Kitaigorodsky (1973) was able to say: 'using as substituents in benzene, halogen atoms, methyl groups and other small radicals, one can obtain a large number of isomorphous crystals of the hexachlorobenzene type, *i.e.* centrosymmetric monoclinic structure $P2_1/c$ with two molecules per unit cell'. Attention was highly focused 50 years ago on the HSB of the general formula $C_6X_nY_{6-n}$ (X and Y being halogens or methyls), when White, Biggs & Morgan (1940) discovered that their real permittivity ϵ' was as high in the crystalline state as in the liquid state. They also found that the polar compounds exhibited high dielectric losses characteristic of the Debye relaxation theory, so they assumed that molecules quickly jump in the crystals over a large temperature range below freezing point. The pioneering work of Tulinsky & White (1958) established by X-rays that 1,2-dichloro-3,4,5,6-tetramethylbenzene or dichloroprehnitene (DCP) exhibited an amazing disordered structure at room temperature: it crystallizes in the monoclinic system $P2_1/c$, with two molecules per unit cell, as in hexachlorobenzene, but if the C atoms of the benzene rings are well located around a center of symmetry, more unexpected was the fact that in the final three-dimensional electron-density diagram, the six substituent peaks were of the same magnitude. Thus, electron density was consistent with an occupancy probability of 0.33 for a chlorine and of 0.67 for a methyl near each aromatic carbon. Tulinsky & White (1958) also found that molecules possess large anisotropic thermal vibrations in accordance with rigid-body torsional vibrations mainly around their sixfold axis: remembering the fact that the dielectric properties of DCP were frequency dependent in the kilocycle region and that the intensity of the maximum dielectric losses required motion of all the dipolar molecules, they concluded that

the random distribution was clearly due to a dynamic phenomenon. The disordered structure of DCP was thus the prototype of the bidimensional-rotational crystalline state observed with discoïd molecules, a specific case of 'orientational disorder in crystals' (ODIC), or of 'plastic crystals'.

Indeed, following Tulinsky's work, many HSB structures were established. In general, the situation at room temperature seems similar to that of DCP: the benzene ring is well located and the electron density located by X-rays gives an average molecule which displays $6/mmm$ symmetry. Hence, the structure found reveals the disorder of the molecular packing, *i.e.* among others, the case of 13 bromochlorobenzenes, $C_6Cl_nBr_{6-n}$ (Khotsyanova, 1966). However, if there are substitutions by F atoms, it depends: for C_6Cl_3F , Khotsyanova, Robas & Semin (1964) or Babushkina *et al.* (1967) found a disordered structure, while in the case of C_6Br_5F order began: among the six positions around the benzene ring, two are preferentially occupied by F atoms at room temperature, while the order is total at 77 K. Among the polyhalogenobenzenes, 1,3,5-trichloro-2,4,6-trifluorobenzene (Chaplot, McIntyre, Mierzejewski & Pawley, 1981) exhibits very peculiar behavior. This molecule belongs to hexagonal $P6_3/m$ space group, with molecules at sites respecting the symmetry of the isolated molecule; it is not likely that the threefold symmetry of the molecule is still found locally in the crystalline cell. When the substituents are of very different sizes, *e.g.* fluorine and iodine, the molecules are fixed in the cell and no disorder is found at room temperature, which is the case for *para*-dibromo- and *para*-diiodotetrafluorobenzene (Pawley, MacKenzie & Dietrich, 1977). From the change in halogen quadrupolar resonance frequency, Babushkina (1966) and Khotsyanova, Babushkina & Kuznetsov (1969) demonstrated that all these compounds exhibit phase transitions, the highest temperature phase always being dynamically disordered. Nevertheless, it seems that no work has been carried out on the structures of the stable phases at temperatures sufficiently low for order in all the molecules.

At room temperature, almost all the halogenomethylbenzenes $C_6X_n(CH_3)_{6-n}$ also belong to the monoclinic space group $P2_1/c$, $Z=2$. In particular, the compounds 2,4,5,6-tetrabromo-1,3-dimethylbenzene (I) (Strel'tsova & Struchkov, 1961), 1,2,4-trichloro-3,5,6-trimethylbenzene (II) (Charbonneau & Trotter, 1967), pentabromotoluene (III) (Krigbaum & Wildman, 1971), pentachlorotoluene (IV), 1,2,3,5-tetrachloro-4,6-dimethylbenzene (V) and 1,2,4,5-tetrachloro-3,6-dimethylbenzene (VI) (Khotsyanova, Babushkina, Kuznetsov & Semin, 1972), 1,2,3-trichloro-2,4,6-trimethylbenzene (VII) (Fourme, Renaud & André, 1972) and 1,4-dichloro-2,3,5,6-tetramethylbenzene (VIII) (Messenger & Blot, 1971). Studies of line width

and second moment in NMR, as well as Hertzian dipolar absorption have provided evidence that, at room temperature, the molecules of almost all these compounds jump between equivalent sites *via* $2\pi/6$ jumps in the molecular plane; see White, Biggs & Morgan (1940), Eveno & Meinel (1966), Balcou & Meinel (1966) for II and VIII, Brot & Darmon (1966) for IV, Brot, Darmon & Dat-Xuong (1967) for VII and DCP. In all these cases, the molecular motion slows down as the temperature decreases and the motion is generally locked below 150 K or before. However, an outstanding query asks what type of structure exists at very low temperature? Is the disorder frozen or does an ordered phase appear?

Fourme, Renaud & André (1972), studying the trichloro compound (VII) at 173 K, have found that the dipolar molecules adopt an antiparallel disposition which at low temperature leads to a doubling in the *b* and *c* parameters of the high-temperature cell. In the case of the dichloro compound (VIII) at 70 K, Messenger, Cailleau & Yelon (1978) observed an ordering of the quadrupolar molecules leading to a tripling of parameter *b* and a doubling of *a* in the $P2_1/c$ cell. Thereafter, it was accepted that low-temperature cells correspond to well ordered crystals. In some cases, the ordering already starts at room temperature. The first example was found by Charbonneau, Sanquer & Meinel (1967), who observed that chloropentamethylbenzene belongs to the monoclinic $P2/m$ system with two molecules per cell. The structure is disordered, but there are different occupation rates for the chlorine between the six positions around the benzene ring. A similar structure is adopted by bromo- and iodopentamethylbenzene. From NMR (Eveno & Meinel, 1966), dielectric absorption (Balcou & Meinel, 1966) and calorimetric measurements (Lagarrigue, 1972, 1973; Gyoten, Yoshimoto, Atake & Chihara, 1982) it was established that such compounds undergo phase changes, the molecules stopping their motion and adopting an ordered arrangement in the low-temperature phase.

Hexamethylbenzene (HMB) deserves a special mention: it crystallizes in the triclinic system $P\bar{1}$, with one molecule per cell located around the center of symmetry. Hamilton, Edmonds, Tippe & Rush (1969) localized H atoms by neutron diffraction at 130 K. At the same time, Allen & Cowking (1967) established that molecules jump in their planes in phases I and II above 116 K, while the methyl groups always 'jump' even in phase III from 116 K to below 4 K. For this compound it is difficult to calculate the interactions between the numerous methyl groups; so many authors made the assumption that the intramolecular interactions were widely dominating (Hamilton, Edmonds, Tippe & Rush, 1969; Takeda, Fujiwara & Chihara, 1989). This conclusion was justified by atom-atom interaction calculations, a treatment which is open to much criticism, as we

have demonstrated recently (Meinel, Mani, Tonnard, Nusimovici & Sanquer, 1993). It has also been shown recently (David, Glazer, Ibberson & Inaba, 1992) that HMB is rhombohedral pseudo-cubic ($\alpha = 90.155^\circ$) at 4 K with the benzene ring planar and the ring-methyl links being slightly puckered with an angle of 0.96° with the ring plane.

As our final objective is the study of the tunneling behavior of the methyl groups at low temperature, we justify the choice of 1,3,5-trichloro-2,4,6-trimethylbenzene or trichloromesitylene (TCM) for structural studies by several points: (1) there are no adjacent methyl groups in the molecule, and thus intermolecular effects are more easily distinguishable from intramolecular effects than in HMB; (2) in similar compounds (Chaplot, McIntyre, Mierzejewski & Pawley, 1981), molecules with a threefold axis of symmetry show specific behavior from a crystallographic viewpoint; (3) during our work Takeda, Fujiwara & Chihara (1989), studying the compound by NMR and calorimetric measurements, have confirmed its physical properties; (4) we were able to perform tunneling spectroscopy of the methyl groups of TCM and found unusual and rich features (Meinel *et al.*, 1992).

2. Experimental

Synthesis of the material and crystal growth

The material was synthesized in the laboratory by direct chlorination of 1,3,5-trimethylbenzene (mesitylene) in the presence of pyrophoric iron as a catalyst. Pyrophoric iron was made *in situ*, at 973 K, by decomposition of ferrous oxalate in the presence of hydrogen. Mesitylene (10 g) was diluted in purified CCl_4 (200 g) and placed into a balloon in a refrigerator. The mixture was heated to 303 K and chlorine carried by a nitrogen stream was then passed through the solution. The chlorination reaction was controlled by extracting periodic samples, which were analysed by gas chromatography. The raw material obtained was purified by two successive recrystallizations of CCl_4 solutions at 277 K. A further sublimation gave TCM with the freezing point 484 ± 1 K, with less than 0.3% dichloromesitylene as the main impurity. Crystals were prepared by slow evaporation of a saturated solution in benzene at 293 K. Lengthy needles grew along the *a* axis, generally twinned. Single crystals were chosen after a polarizing microscope inspection.

Data collection

In a parallelepiped needle we cut an approximately cubic sample, measuring $0.3 \times 0.3 \times 0.3$ mm³. Preliminary studies at 297 ± 2 and 150 ± 5 K have shown that at these temperatures, crystals belong to

Table 1. Evolution of refinement as a function of the isotropic thermal parameter attributed to the H atoms

$B(H)$ (\AA^2)	3	4	5	6	7	8	9	10	11	12
R (%)	3.7	3.6	3.5	3.5	3.4	3.4	3.4	3.4	3.5	3.5
wR (%)	5.5	5.3	5.1	5.0	5.0	4.9	4.9	5.0	5.0	5.0
D	2.167	2.106	2.044	2.005	1.983	1.961	1.970	1.974	1.983	1.994
u^2	0.038	0.051	0.063	0.076	0.0879	0.101	0.114	0.127	0.139	0.152

the triclinic system. Intensity data were collected on an Enraf–Nonius CAD-4F automatic diffractometer with graphite-monochromatized Mo $K\alpha$ radiation. The scanning mode was $\omega/2\theta$. No significant intensity variation for standard reflections was observed; data were corrected for Lorentz–polarization effects, but not for absorption. The recording domain was limited by $-8 \leq h \leq 8$, $-9 \leq k \leq 9$, $0 \leq l \leq 9$. The unit-cell dimensions were refined using 25 independent Bragg reflexions.

Calorimetric measurements (Fujiwara, Atake & Chihara, 1990) revealed on heating a first-order phase transition around $T_i = 151$ K and a large hysteresis domain in temperature, so phase III can be observed more than 20 K below T_i . We, however, took the insurance that we always remained in phase III by the fact that the reference reflections did not vary in accordance with time.

Structure solution and refinements

The structure was solved (except hydrogens) by direct methods using the *MULTAN* program (Germain, Main & Woolfson, 1971). The positions of the C and Cl atoms were easily deduced from the most probable set of phases. The hydrogens were then located on a difference Fourier map.

Structure refinement was performed in the same way for both the 150 and 297 K data. The function minimized in the full-matrix least-squares program (LSFM; Structure Determination Package, 1981) was $\sum w(F_o^2 - F_c^2)$, where $w^{-1} = \sigma^2(F_o^2) + (0.04F_o^2)^2$. Three cycles of refinement were performed. In the final cycle at 150 and 297 K (in square brackets), 278 [428] reflections with $I < 3\sigma(I)$ were rejected as unobserved, leaving 1222 [1074] reflections in the least-squares calculations for the refinement of 137 parameters: one scale factor, 63 positional parameters, 72 anisotropic thermal parameters for non-H atoms, one isotropic thermal factor for H atoms fixed at 150 and 297 K to 2 and 4\AA^3 , respectively, and one isotropic extinction coefficient. The final agreement factors at 150 and 297 K (in square brackets) are: $R = 0.035$ [0.038] and $wR = 0.047$ [0.051]. The e.s.d. of an observation of unit weight at 150 and 297 K (in square brackets) is $D = 1.995$ [1.647] with $D = w(|F_o| - |F_c|)^2(N_o - N_v)^{-1}$, where N_o is the number of observed reflexions and N_v is the number of variable parameters.

In a further step the C—H bond lengths and hydrogen thermal factors were refined, the isotropic thermal factor for the H atoms being fixed at 150 and 297 K to 2 and 4\AA^2 , respectively; at this stage we found large discrepancies in the apparent C—H bond lengths computed. We

then undertook another study of hydrogen parameters while imposing a trigonal symmetry on the methyls, which is physically more valuable than using variable C—H bond lengths. Firstly, we used variable isotropic thermal factors while the C—H length was fixed to 0.95 \AA and the methyl carbon estimated tetrahedral. The reliability factor varies slightly when B is varied from 3 to 12\AA^2 (Table 1), a minimum appearing between 8 and 9\AA^2 . This is a rather large value, but NMR shows that at 150 K the reorientational motion of the molecules is just beginning to slow down, therefore, B values must be large due to easy molecular librations. In a second step, we adopted $B = 8 \text{\AA}^2$ and allowed the C—H bond length to vary between 0.75 and 1.05 \AA by steps of 0.05 \AA ; a flat minimum of the agreement factor R was found in the region 0.85–0.95 \AA . For C—H = 0.90 \AA and $B = 8 \text{\AA}^2$, the reliability factors are $R_1 = 3.4$ and $R_2 = 4.9\%$, which is rather satisfactory. The apparent short bond length must be associated with the high B value; no correction was attempted in such conditions.

3. Results and discussion

Tables 2(a) and (b) list the refined atomic positional parameters of the non-H atoms, associated anisotropic thermal parameters and isotropic equivalent thermal parameters at 150 and 297 K (in square brackets). Tables 3 and 4 show the corresponding bond lengths and angles.* Atomic positions found at 297 K are very close to those at 150 K, while the isotropic equivalent thermal parameters at 297 K are almost twice those computed at 150 K, which is expected. The molecule is represented in Fig. 1 with thermal ellipsoids at 150 K. The mean values for bond lengths are at 150 K [297]: $C_{ar}-C_{ar} = 1.392$ (3) [1.389 (4)], $C_{ar}-C_m = 1.500$ (3) [1.505 (4)], $C-Cl = 1.750$ (3) \AA [1.745 (2)]. In unpublished work by Tsujita & Yasuoka, quoted in Takeda, Fujiwara & Chihara (1989), the values found at room temperature were very close to these values: $C_{ar}-C_{ar} = 1.394$, $C_{ar}-C_m = 1.525$, $C-Cl = 1.743$ \AA . At 150 K, as at 297 K, we found a significant deformation of the angles of the benzene ring from a regular hexagon: the mean endocyclic angle is 124.5 (2) $^\circ$ near the carbon bearing a chlorine,

* Lists of structure factors, H-atom coordinates and bond lengths involving H atoms have been deposited with the IUCr (Reference: PA0298). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. Fractional atomic coordinates and temperature factors

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> ₁₁	<i>B</i> ₂₂	<i>B</i> ₃₃	<i>B</i> ₁₂	<i>B</i> ₁₃	<i>B</i> ₂₃	<i>B</i> _{eq}
(a) 150 K										
C1	0.2613 (3)	-0.1105 (3)	-0.0705 (3)	1.56 (9)	1.97 (7)	2.01 (7)	-0.11 (6)	-0.62 (5)	-1.24 (5)	1.67 (6)
C2	0.2574 (4)	-0.1840 (3)	0.1115 (3)	1.78 (9)	1.80 (7)	1.88 (7)	-0.28 (6)	-0.51 (6)	-0.81 (5)	1.82 (6)
C3	0.2459 (4)	-0.0636 (3)	0.1753 (3)	1.71 (9)	2.11 (8)	1.57 (7)	-0.21 (6)	-0.64 (6)	-0.76 (5)	1.77 (6)
C4	0.2368 (3)	0.1196 (3)	0.0696 (3)	1.43 (9)	2.06 (7)	1.89 (7)	-0.26 (6)	-0.49 (6)	-1.03 (5)	1.71 (6)
C5	0.2442 (4)	0.1791 (3)	-0.1118 (3)	1.90 (3)	1.59 (8)	1.96 (7)	-0.20 (6)	-0.58 (6)	-0.70 (5)	1.86 (6)
C6	0.2551 (3)	0.0710 (3)	-0.1885 (3)	1.56 (9)	2.01 (8)	1.65 (6)	-0.23 (6)	-8.59 (6)	-0.83 (5)	1.70 (6)
Cl1	0.2763 (1)	-0.25580 (7)	-0.15747 (7)	3.11 (3)	2.18 (2)	2.35 (2)	-0.31 (2)	-0.96 (1)	-1.43 (1)	2.30 (2)
Cl3	0.2391 (1)	-0.14740 (8)	0.40398 (7)	3.41 (3)	2.53 (2)	1.48 (2)	-0.44 (2)	-1.02 (1)	-0.77 (1)	2.41 (2)
Cl5	0.2383 (1)	0.40746 (8)	-0.25393 (8)	4.53 (3)	1.57 (2)	2.22 (2)	-0.44 (2)	-1.46 (2)	-0.46 (1)	2.78 (2)
C _m 2	0.2678 (4)	-0.3797 (3)	0.2315 (3)	4.00 (10)	1.92 (8)	2.55 (8)	0.55 (8)	-1.52 (7)	-0.67 (6)	2.72 (7)
C _m 2	0.2230 (4)	0.2433 (3)	0.1453 (3)	3.90 (10)	2.54 (8)	2.05 (7)	-0.29 (7)	-0.70 (6)	-1.34 (5)	2.39 (7)
C _m 6	0.2627 (4)	0.1440 (3)	-0.3857 (3)	3.30 (10)	2.34 (8)	1.87 (7)	-0.09 (7)	-1.17 (6)	-0.99 (5)	2.40 (7)
(b) 293 K										
C1	0.2624 (4)	-0.1099 (3)	-0.0704 (3)	3.30 (10)	3.95 (8)	3.61 (8)	-0.34 (8)	-1.19 (7)	-2.28 (5)	3.30 (7)
C2	0.2601 (4)	-0.1841 (3)	0.1112 (3)	3.40 (10)	3.54 (9)	3.56 (8)	-0.28 (8)	-1.26 (7)	-1.71 (6)	3.38 (7)
C3	0.2473 (4)	-0.0643 (4)	0.1741 (3)	3.20 (10)	4.05 (9)	2.93 (7)	-0.54 (8)	-1.24 (7)	-1.64 (6)	3.21 (7)
C4	0.2357 (4)	0.1161 (3)	0.0710 (3)	3.10 (10)	4.11 (9)	3.37 (8)	-0.70 (7)	-0.37 (7)	-2.16 (5)	3.26 (7)
C5	0.2417 (4)	0.1773 (3)	-0.1091 (4)	3.60 (10)	3.22 (9)	3.57 (8)	-0.47 (8)	-1.23 (7)	-1.50 (6)	3.38 (7)
C6	0.2553 (4)	0.0698 (4)	-0.1861 (3)	3.10 (10)	4.12 (9)	3.10 (7)	-0.35 (8)	-1.20 (7)	-1.86 (6)	3.22 (7)
Cl1	0.2801 (1)	-0.2532 (1)	-0.1577 (1)	6.30 (4)	4.72 (2)	4.94 (2)	-0.56 (2)	-1.99 (2)	-3.16 (1)	4.75 (2)
Cl3	0.2410 (1)	-0.1486 (1)	0.4014 (1)	6.47 (4)	5.50 (3)	3.10 (2)	-0.93 (3)	-1.96 (2)	-1.74 (2)	4.86 (2)
Cl5	0.2319 (1)	0.4040 (1)	-0.2483 (1)	8.62 (5)	3.35 (3)	4.79 (3)	-0.76 (3)	-2.93 (3)	-1.19 (2)	5.55 (3)
C _m 2	0.2699 (5)	-0.3786 (4)	0.2296 (4)	7.20 (20)	3.70 (10)	4.50 (10)	-0.90 (10)	-2.40 (10)	-1.29 (8)	5.10 (10)
C _m 4	0.2227 (5)	0.2400 (4)	0.1464 (4)	4.90 (10)	4.72 (9)	4.83 (9)	-0.21 (9)	-1.67 (8)	-3.23 (6)	4.29 (8)
C _m 6	0.2586 (5)	0.1423 (4)	-0.3815 (4)	5.50 (20)	4.50 (10)	3.25 (9)	0.30 (10)	-1.58 (9)	-1.87 (7)	4.49 (9)

Table 3. Bond lengths (Å)

	150 K	297 K
Cl1—C1	1.750 (2)	1.742 (4)
Cl3—C3	1.750 (2)	1.749 (3)
Cl5—C5	1.750 (2)	1.744 (2)
C1—C2	1.388 (3)	1.396 (4)
C1—C6	1.398 (3)	1.390 (3)
C2—C3	1.395 (3)	1.391 (5)
C2—C _m 2	1.497 (3)	1.495 (4)
C3—C4	1.394 (3)	1.379 (3)
C4—C5	1.393 (3)	1.391 (4)
C4—C _m 4	1.499 (3)	1.511 (5)
C5—C6	1.386 (3)	1.386 (5)
C6—C _m 6	1.504 (3)	1.509 (4)

Table 4. Bond angles (°) at 150 and 293 K

	150 K	207 K
Cl1—C1—C2	117.5 (2)	117.5 (2)
Cl1—C1—C6	118.0 (1)	118.2 (2)
C2—C1—C6	124.4 (2)	124.3 (3)
C1—C2—C3	115.7 (2)	115.3 (3)
C1—C2—C _m 2	122.4 (2)	122.2 (3)
C3—C2—C _m 2	121.9 (2)	122.5 (3)
Cl3—C3—C2	118.0 (2)	117.6 (2)
Cl3—C3—C4	117.6 (2)	117.8 (3)
C2—C3—C4	124.3 (2)	124.6 (3)
C3—C4—C5	115.3 (2)	115.9 (3)
C3—C4—C _m 4	122.2 (2)	122.3 (3)
C5—C4—C _m 4	122.5 (2)	121.8 (2)
Cl5—C5—C4	117.7 (2)	118.2 (3)
Cl5—C5—C6	117.3 (2)	117.5 (2)
C4—C5—C6	124.9 (2)	124.3 (2)
C1—C6—C5	115.3 (2)	115.6 (3)
C1—C6—C _m 6	122.5 (2)	121.9 (3)
C5—C6—C _m 6	122.2 (2)	122.5 (2)

while it is 115.5 (2)° for the carbon bearing a methyl (Fig. 2a). Therefore, it is the angle nearest the carbon bearing the most electronegative substituent which is the largest; this result is in accordance with systematic trends established by Domenicano & Murray-Rust (1979) and

Domenicano, Vaciago & Coulson (1975). From the structural results of 71 derivatives, they established the characteristic effects of 21 substituents on the internal angles of the ring of mono- or *para*-disubstituted benzene compounds. Using the notation in Fig. 3, the deviations from 120° found for the angles α , β , γ and δ are: for methyl substitution: -1.9 (2), 1.0 (1), 0.4 (1) and -0.8 (2)°; for chlorine substitution: 1.9 (1), -1.4 (1), 0.6 (1) and -0.2 (2)°. Using these values and assuming linear additivity of the substituent interactions in the

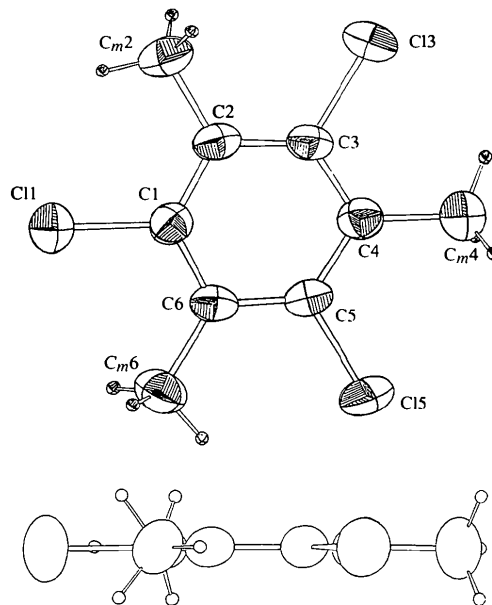


Fig. 1. View of the molecule showing the atom-numbering scheme. Thermal ellipsoids are drawn at the 30% probability level.

first stage, an angle of 124.2° facing a chlorine and conversely 115.8° facing a methyl was calculated. These values are very close to those experimentally found.

Fig. 4 shows a projection along c onto the ab plane, with molecules stacked up along the tilted a axis in a tidy antiferroelectric manner due to the presence of a center of symmetry halfway between the two molecules of the unit cell; the inversion centers are located at (000) and $(\frac{1}{2}00)$. As for many other benzene compounds, the stacking of molecules along the a axis is consistent with the fact that the thermal expansion is more important in that direction than in the (100) plane. In a projection normal to the molecular plane, each row is moved back from the preceding one by *ca* 0.6 \AA , a quantity corresponding to a little less than half an aromatic ring width (Fig. 5). It is to be noted that in the case of the hexamethylbenzene, the second sheet of molecules due to the translation along the a axis corresponds in projection to a displacement of 1.33 \AA , a value noticeably different to that found for TCM and corresponding to another type of packing. Conversely, for 1,3,5 trichloro-2,4,6-trifluorobenzene, Chaplot, McIntyre, Mierzejewski & Pawley (1981) found that the molecules are perpendicular

to the hexagonal c axis and arranged in a regular hexagonal cell.

With regard to the orientation of the molecules projected onto the bc plane, we would like to draw attention to the fact that the molecular axis through Cl15 and the three carbons C5, C2 and C_{m2} is almost perpendicular to the projection of the a axis (Fig. 5). All four atoms are significantly more shaken than the corresponding atoms along the two other diad axes deduced by a rotation of $+60^\circ$, as can be seen from the equivalent isotropic thermal factors in Table 2. The significant discrepancies between the isotropic temperature factors for the same atoms located on different axes are indicative of a large anisotropy of the intermolecular force field seen by the different regions of the molecular entity; it is also related to other physical observations. Firstly, splitting into three different lines for the quadrupolar resonance frequency of ^{35}Cl atoms mentioned by Babushkina, Robas & Semin (1967) at 77 K, and observed from 77 to 244 K by Groke (1992). Secondly, the fact that Meinel *et al.* (1992) studying the tunneling of the methyl rotors by neutron spectroscopy found three different values for the splitting of the ground state provides evidence for

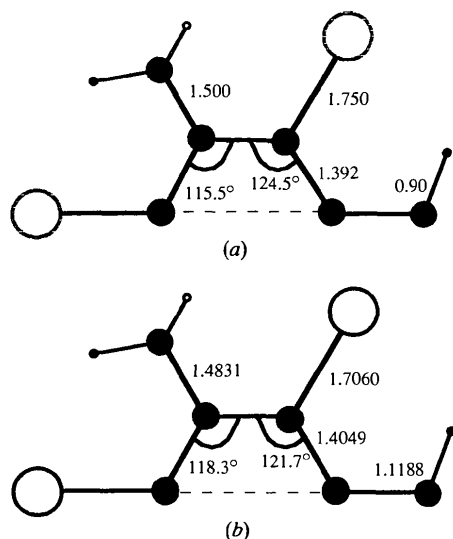


Fig. 2. Comparison of the mean bond lengths (\AA) and angles ($^\circ$) found from (a) X-rays and (b) the quantum chemistry program AM1.

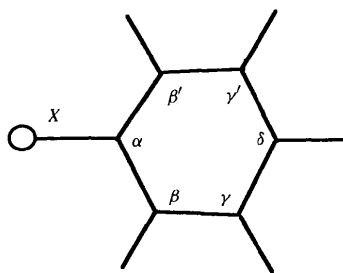


Fig. 3. Angles for the study of the influence of substituent X.

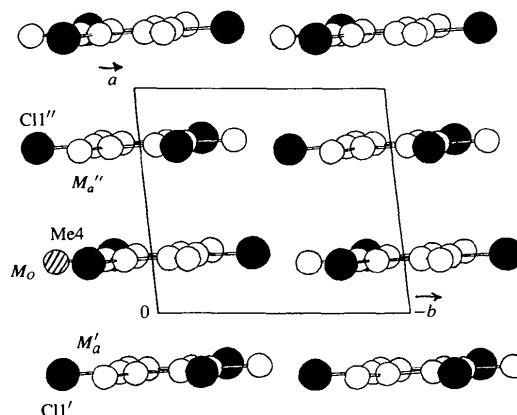


Fig. 4. The packing of $\text{C}_6(\text{CH}_3)_3\text{Cl}_3$; projection onto the bc plane down the c axis.

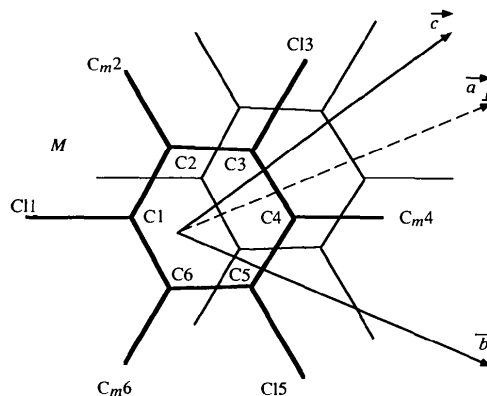


Fig. 5. Orthogonal projection of the two molecules M_o and $M_{a''}$ of Fig. 4 onto the bc plane.

the nonequivalence of the hindering potentials seen by the three methyls of each molecule. It is then of great interest to discover more precisely how the H atoms are localized and how their positions evolve according to temperature. Another interesting fact is that all heavy atoms of the molecule are at 150 and 297 K, respectively, situated in the mean molecular plane P of the equations: $0.9284x - 0.2284y - 0.2931z = 2.4323$ and $0.9319x - 0.2136y - 0.2931z = 2.4918$, where x , y and z are given in relation to an orthogonal set of axes based on b' , c' and a' , given by $b' = b$, $c' = a \wedge b$ and $a' = b \wedge c'$. Therefore, the molecular plane is very close to the (100) plane, the dihedral angle between them being only 3.4° . It is dangerous at this stage of the refinement to assert puckering of the molecule as the refinement of individual atoms does not account for the rigid-body motion of the cycle, which gives rise to curvilinear displacements of the substituents. For the high-temperature structure, the deviations out of the molecular plane amount to 0.009 \AA for C15 and C4, while they are smaller than 0.005 \AA for all the other carbons and chlorines. As these apparent out-of-plane deviations do not respect the threefold symmetry axis, we believe that they are not significant and, therefore, we were not able to confirm the hypothesis of Takeda, Fujiwara & Chihara (1989), who assumed an out-of-plane deformation similar to that given by Hamilton, Edmonds, Tippe & Rush (1969) for hexamethylbenzene. At this stage, we tried to progress by a theoretical approach of the isolated molecular geometry and an evaluation of the packing forces in the crystal.

4. Theoretical chemistry computations of the isolated molecular geometry

Our final goal being the comprehension of the tunneling for the three methyl groups, it is necessary to test theoretical programs computing molecular geometry in order to locate more precisely the positions of the hydrogens in the isolated molecule and, consequently, the height of the potential barrier hindering the methyl group rotation. We used the *AM1* method (Austin Model 1) perfected by Dewar, Zoebisch, Healy & Stewart (1985), which is a semi-empirical method derived from the *MNDO* method (Modified Neglect of Differential Overlap) developed by Dewar & Thiel (1977). A mathematical process for geometry optimization is associated with such methods. Compared with *MNDO*, changes introduced in *AM1* allow conjugation effects to counterbalance the repulsion due to steric effects. We used the *MOPAC* program of Stewart (1989), after testing with highly conjugated molecules (Hamdellou, 1989). In an initial stage for TCM, we used the geometry found for heavy atoms by X-rays at 150 K, while for each methyl we chose a configuration where one hydrogen remained in the molecular plane, and assumed a regular tetrahedral symmetry for

Table 5. *Interaction coefficients used for the determination of the crystalline potential and the phonon frequencies using a Buckingham-type atom-atom potential*

Unit	A_{ij} (kJ mol ⁻¹ Å ⁶)	B_{ij} (kJ mol ⁻¹)	C_{ij} (Å ⁻¹²)
C—C	-2142	299 905	3.60
C—H	-493	35 526	3.67
C—Cl	-5164	70 709	2.93
H—H	-102	9070	3.74
Cl—H	-1126	12 715	3.00
Cl—Cl	-12 450	19 135	2.26

the methyl groups. We then released bond lengths and molecular angles (except methyl angles) so as to find the best set of variables minimizing the computed enthalpy of formation ΔH_f of the compound. We then proceeded step-by-step, turning the control methyl group by 5° steps, while the two other methyls were allowed to rotate so as to find the lowest minimum of ΔH_f . It appears that the configuration, with one C—H bond for each methyl in the molecular plane and a trigonal symmetry for the whole molecule, is the most favorable and gives the lowest ΔH_f . Such a result indicates a correlation in the orientations of the methyls, which significantly favors a true trigonal symmetry for the whole molecule. The bond lengths we obtained using *AM1* after optimization of the geometry are: $C_{ar}-C_{ar} = 1.4049$, $C-Cl = 1.7060$, $C_{ar}-C_m = 1.4831$ and $C-H = 1.1188 \text{ \AA}$. For the calculations, the geometry of the ring is significantly less distorted than for our X-ray experiment. The angles in the benzene ring are only 121.7° near the carbon bearing a chlorine, and 118.4° for the carbon facing a methyl group, Fig. 2(b). However, qualitatively the *AM1* results are in good agreement with the X-ray structural determination as the calculated ring angle is significantly enlarged when the aromatic carbon is linked to an electronegative substituent. On an absolute scale, the calculated deviations from 120° are approximately half those found by X-rays, while the C—H bond is a little larger and the C—Cl bond smaller than generally quoted in crystallography (1.706 \AA for *AM1*; 1.740 \AA in general; 1.750 \AA from our X-ray data). We must remember that our experiments concern highly shaken molecules; it seems desirable to study the structure at much lower temperature, before pursuing the comparison between experiment and theory.

In order to compute the potential hindering reorientation of one methyl, we used the most stable configuration obtained by *AM1* as a starting point, and fixing all other atoms we studied the variation in energy formation while rotating the control methyl around its threefold axis. We found a difference ΔU_{int} of ca 2.9 kJ mol^{-1} between the extrema; this value is close to 2.4 kJ mol^{-1} found by Takeda, Fujiwara & Chihara (1989) using NMR, and assigned to the barrier height seen by the methyls. However, we believe that Takeda has improperly extended the use of atom-atom potentials to the calculus of the

Table 6. Comparison of the calculated and observed frequencies in IR absorption, and Raman and neutron scattering

Neutron scattering	ν_{exp}	(cm^{-1})		28	36	46	55	74	78	83	96	117	
Raman observed	ν_{lat}	(cm^{-1})		25	33		54					—	
Raman calculated	ν_{lat}	(cm^{-1})		21	25	32	33	57				107	
IR observed	ν_{lat}	(cm^{-1})	0	0	0				70		83	95	119
IR calculated	ν_{lat}	(cm^{-1})	0	0	0						90	96	
IR calculated	ν_{int}	(cm^{-1})						41		76	80		

intramolecular interactions, as this method has to be used only for interactions between nonbonded atoms, which is not the case in aromatic molecules (Meinell *et al.*, 1992). In our treatment, we must also take into account the contribution to the hindering potential due to the environment, which is possible as we are able to appreciate the van de Waals forces due to the interaction of the molecules in the crystal, from the crystalline structure.

5. Molecular packing, potentials hindering the molecular reorientation and phonon frequencies

Experiments and calculus from atom–atom interactions

For a long time, it has been well known that it is possible to compute the physical properties of crystals, such as phonon spectra, elastic coefficients *etc.*, from atom–atom interaction potentials (Williams, 1967; Kitaigorodsky, 1973; Pertsin & Kitaigorodsky, 1987). To deduce such structural properties for trichloromesitylene, we used a (6-exp) Buckingham potential which can be written as

$$V_{\text{int}} = \sum_{ij} V_{ij} = \sum_{ij} [B_{ij} \exp(-C_{ij}r_{ij}) - A_{ij}r_{ij}^{-6}],$$

the coefficients A_{ij} , B_{ij} and C_{ij} relative to the interaction between atoms i and j are given in Table 5. The interaction coefficients between two hydrogens or two carbons are those used by Williams (1972); the coefficients for interactions between chlorines are those adopted by Mirsky & Cohen (1978) in their study of 1,3,5-trichlorobenzene. Each A_{ij} is taken as being the geometric mean between A_{ii} and A_{jj} , similarly for B_{ij} , while C_{ij} is the arithmetic mean of C_{ii} and C_{jj} . Using these coefficients and taking for each atom an influence sphere of *ca* 20 Å, which corresponds for TCM to 135 molecules around the control molecule, we first tested the consistency of the model by verifying the fact that the computed potential corresponds to the structure found by X-rays. The minimum potential $V_o = -151 \text{ kJ mol}^{-1}$ and the best solution is actually very similar to the configuration from X-rays. Using the same potential, we calculated the phonon frequencies at the center of the Brillouin zone and compared the results with the frequencies detected in Raman scattering, IR absorption and neutron scattering. As shown in Table 6, there is generally good agreement between the calculated and experimental values, a fact which installs confidence in the coefficients used for the atom–atom interactions. A more

detailed presentation of the spectroscopic results will be published elsewhere (Nusimovici *et al.*, 1995). Indeed, the analysis warrants some caution since in the range 10–120 cm^{-1} there are 16 characteristic frequencies: nine lattice modes, two degenerate internal modes (out-of-plane deformations) and three torsional excitations of the methyls; almost all have been seen experimentally (Table 6).

Starting from the most stable structure, we then studied the potential variations while one molecule is rotated in its plane around its C_3 axis of symmetry. The molecular potential found, shown in Fig. 6, may be written as

$$V(\Theta) = V_o + V_3[1 + \cos(3\Theta - \Phi)] + V_6(1 + \cos(6\Theta)),$$

with $2V_3 = 6.6$ and $2V_6 = 25.6 \text{ kJ mol}^{-1}$, and the phase $\Phi = 33^\circ$, so that it presents a minimum every 60° , with three of them being deeper by 5.5 kJ mol^{-1} ; the barrier height, or more precisely $V_s = V_3 + V_6$, amounts to 32 kJ mol^{-1} . This result is in good agreement with NMR and X-ray observations: X-rays show a structure without disorder, while NMR (Takeda, Fujiwara & Chihara, 1989; Tazi, 1990) indicates that the molecules jump in their planes, and thus our computations are consistent with preferential jumps of $2\pi/3$ and not $2\pi/6$ as in many other hexasubstituted benzenes reviewed in the *Introduction*. This is due to the ternary symmetry of the molecule, which means that the jumps by $2\pi/3$ cannot be revealed by X-ray diffraction. On the other hand, the fact that the potential hindering the molecular reorienta-

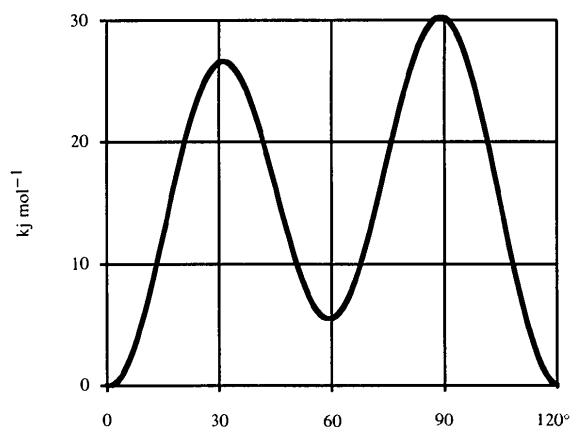


Fig. 6. Potential hindering the molecular reorientation as calculated with the Buckingham potentials of Table 5.

tion produces the term $V_6[1 + \cos(6\Theta)]$ for the main component is a consequence of three factors: (1) the molecule jumps in the molecular plane which is in close proximity to the bc plane; (2) angle α in bc is practically 60° , so that each molecule is surrounded by six similar molecules in a quasi-regular hexagonal array; (3) the 'control' molecule which is rotated has a true ternary symmetry, but furthermore the blocking volume of a Cl atom is similar to that of a methyl group. The computed value of 32 kJ mol^{-1} is smaller than 43 kJ mol^{-1} given by NMR; this discrepancy may be partly due to the fact that we have used the structure found at 150 K, while the frequencies were calculated at 0 K.

6. Calculus of the barriers hindering methyl tunneling

Knowing the atomic positions for the molecules in their deeper potential well, we were able calculate the contribution of each methyl to the barrier due to intermolecular interactions. We will present here only the main features; a detailed comparison with the experiment will be published separately (Nusimovici *et al.*, 1995). For the potential hindering the tunneling of one methyl, specific chlorines in the eight adjacent molecules play the most important role. On the one hand, note the Me4 methyl characterized by C_m4 of the molecule M_o in Fig. 4; the Cl11 belonging to the two molecules M_a' and M_a'' , deduced from the molecule M by the action of the symmetry centers located on the a axis, contributes roughly in $\cos 6\varphi$ to the potential acting on Me4 as their influences are out of phase and almost equal. On the other hand, in a bc plane, now note the environment of Me4 in the control molecule M_o . Fig. 7 shows that after a translation equal to $+b$ the molecule M_b is found, in

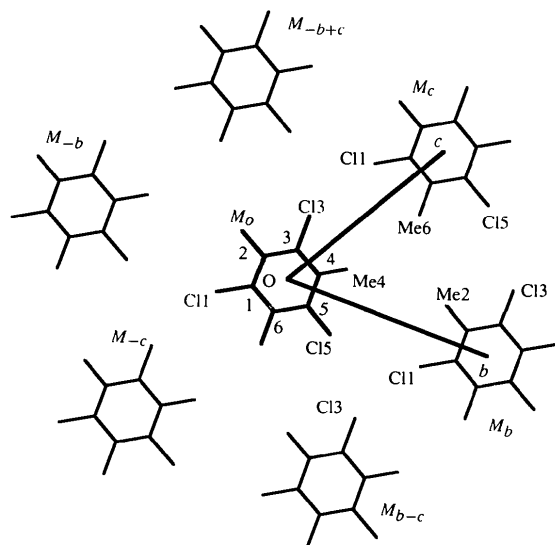


Fig. 7. Labeling of the six nearest neighbors of the molecule M_o in the bc plane.

which Cl11 is the nearest neighbor of Me4 in M_o ; as for the interaction of the molecule M_c due to a translation of M_o by $+c$, the distance from Cl1 to Me4 is larger, thus exerting a smaller influence; therefore, these two Cl atoms contribute to the potential V_{inter} mainly in $\cos 3\varphi$. Finally, this also occurs with Cl5 of the two molecules M_o and M_c acting on Me2 of the molecule M_b , and also with Cl3 of M_o and M_b acting on Me6 of M_c , and thus the total potential has a main component in $V_3 \cos 3\varphi$. The intermolecular contribution to the barrier height found for Me4 is of the order 1.7 kJ mol^{-1} , a little less than the internal contribution to the barrier, computed from AM1. Therefore, we have a quantitative model for solving the Mathieu equation, which gives the tunneling splittings for the three methyls of TCM: using the atom-atom coefficients of Williams (1992) as 2.5 , 5 and $8 \mu\text{eV}$, experimentally by incoherent neutron scattering, Meinel *et al.* (1992) have observed three pairs of excitations of the same intensity lying near 4 , 9 and $13 \mu\text{eV}$ and consistent with three different wells seen in the crystal by the methyls. Therefore, our calculus demonstrates that it is the highly asymmetric packing of the molecules in TCM which produces significantly different barriers for each of the three methyls in one molecule, due to the difference between the intermolecular contributions.

7. Concluding remarks

The structure of TCM is unusual in the hexasubstituted benzene family, as no disorder is apparent at 150 or 297 K. Nevertheless, as NMR proves the existence of molecular jumps throughout this temperature range, we assume that the molecules undergo fast stochastic reorientations in their planes between three undiscernable locations in the crystal. From the structural data presented in this paper and using Buckingham-type atom-atom interactions, we were able to establish by calculus the occurrence of three deep minima seen by a molecule rotated in its plane. The calculus also indicates that three other potential minima exist, shifted by $2\pi/6$ from the preceding one. The existence of these other deep wells may explain the appearance of a phase transition near $T_c = 360 \text{ K}$, the molecules jumping randomly between the six minima above T_c . Furthermore, from our structural determination we were able to calculate the barriers hindering the methyls and explain why the three methyls of TCM give different tunneling splittings.

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Conformation of the Two Potential Antipsychotic Agents (–)-(S)-3-Bromo-5,6-dimethoxy-N-[(1-ethyl-2-pyrrolidiny)methyl]benzamide, FLB 457, and its 2-Hydroxy Analogue, FLB 463

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Abstract

The crystal structures and absolute configurations of two potent dopamine-D₂ receptor antagonists, FLB 457, ‡ (–)-(S)-3-bromo-5,6-dimethoxy-N-[(1-ethyl-2-pyrrolidi-

nyl)methyl]benzamide, and FLB 463, (–)-(S)-3-bromo-5,6-dimethoxy-N-[(1-ethyl-2-pyrrolidiny)methyl]salicylamide, have been determined by X-ray diffraction methods. The crystal structure of FLB 457 was derived from its salt with hydrobromide, C₁₆H₂₄BrN₂O₃⁺Br[–], crystallizing in the orthorhombic space group *P*2₁2₁2₁, *a* = 28.900 (18), *b* = 8.747 (3), *c* = 7.585 (1) Å, *Z* = 4, and FLB 463 from its methylsulfonate salt, C₁₆H₂₄BrN₂O₄⁺CH₃SO₃[–], crystallizing in the monoclinic space group *P*2₁, *a* = 15.264 (5), *b* = 8.087 (4),

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‡ FLB 457 was previously known as 5-bromo-2,3-dimethoxy-N-[(1-ethyl-2-pyrrolidiny)methyl]benzamide.