

The Crystal Structure of Mesitaldehyde-Perchloric Acid 2:1 Adduct

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*The crystal structure of the 2:1 adduct of mesitaldehyde-perchloric acid has been solved using X-ray diffraction data. The structure consists of layers in which hydrogen-bonded mesitaldehyde dimers and perchlorate ions occur in a 1:1 ratio. The planes of symmetry of the dimers and ions are coincident with the mirror planes of space group $P2_1/m$. Alternate layers are related by the 2_1 symmetry element in such a way that the molecular rings are stacked in irregular columns along b . In one column the rings overlap, but in the other an *o*-methyl substituent in one layer overlaps the rings of adjacent layers. Two of the twelve methyl groups in the unit cell appear to be rotating quite freely about the bond joining them to the ring, while two others appear to be best explained as hindered rotation (or disorder).*

In the accompanying paper¹ is given a description of the preparation and characterization of a crystalline adduct obtained from mesitaldehyde and molecular perchloric acid in the molar ratio 2:1.

The physical and chemical properties of the adduct revealed little about its structure. All of the reactions attempted on the adduct led either to the regeneration of mesitaldehyde or to the formation of a derivative obtainable directly from mesitaldehyde. The results indicated, though by no means proved, that the adduct was probably a molecular complex and did not have a covalent bond linking mesitaldehyde moieties.¹ The interesting and unusual composition of the substance appeared to warrant an X-ray crystallographic investigation of its structure. This paper describes the results of such an investigation.

Experimental

The adduct, which decomposes at 149°, readily sublimates at 85° under atmospheric pressure to yield thin monoclinic laths, the axis of elongation being b . From oscillation and equi-inclination Weissenberg photographs taken with Cu $K\alpha$ radiation ($\lambda = 1.5418$ Å.), the following unit cell parameters were determined: $a = 8.43 \pm 0.01$, $b = 6.91 \pm 0.01$, $c = 17.39 \pm 0.03$ Å.; $\beta = 97^\circ 57' \pm 9'$. The indicated precisions are estimated standard deviations. The camera radius was calibrated against NaCl, $a = 5.639$ Å.

The density of the crystalline compound as determined by the flotation method was found to be 1.326 g. cm.⁻³. The calculated density, assuming two units of 2:1 mesitaldehyde-perchloric acid adduct per unit cell, was 1.315 g. cm.⁻³.

The only systematically absent reflections were $0k0$ for k odd. This extinction indicates either space group $P2_1$ or $P2_1/m$. Statistical treatment of the data

by the method of Howells, Phillips, and Rogers² indicated the centrosymmetric space group $P2_1/m$.

Intensity data were collected from two crystals, one of dimensions $0.04 \times 0.16 \times 0.17$ mm., the other $0.03 \times 0.27 \times 1.73$ mm. Each crystal was sealed in a thin-walled capillary of Lindemann glass. Nickel-filtered Cu radiation was used in obtaining unidimensionally integrated equi-inclination Weissenberg photographs of the a -axis zero level and b -axis 0-6 levels. Intensities were measured by a recording microdensitometer having a logarithmic response. The direction of scan was at right angles to the direction of integration by the camera. Within the linear response range of the film, the area above background under the trace of each reflection may be taken as proportional to the integrated intensity.

The intensities are subject to appreciable absorption error, complicated in this case by the position of the crystal against the wall of the capillary. Because of the difficulty of accurately allowing for absorption in this case, no correction was applied.

Of the approximately 2050 unique reflections within that part of the reciprocal lattice accessible under the experimental conditions, only 881 (43%) were observed. This is attributed in part to the rather small cross-sectional area of the crystal and to rather shorter exposures than ordinarily used in these laboratories for collecting intensity data.

Determination of the Structure. If the space group is $P2_1/m$, the two perchlorate groups must lie in special positions with their planes of symmetry coincident with the mirror planes of the space group. Although there are four general positions in $P2_1/m$, the dimensions of the unit cell and the disposition of the symmetry elements virtually assure that the mesitaldehyde groups also lie in the mirror planes. On the other hand, should the space group really be $P2_1$, then one unit of the 2:1 adduct would occupy each of the two general positions.

A sharpened, origin-removed, three-dimensional Patterson synthesis was first computed. There were three outstanding peaks of nearly equal height on the Harker section, $P(u, \frac{1}{2}, w)$. Consideration of possible Cl-O vectors led directly to the selection of one of the peaks as primarily due to a Cl-Cl vector. Most of the nonhydrogen atoms were tentatively located from the remaining Harker peaks assuming the space group to be $P2_1/m$. The general distribution of vectors in the Patterson function provided strong evidence that this was, indeed, the correct space group.

Structure factors were next calculated including only the perchlorate group with parameters estimated from the Patterson synthesis. The resulting reliability index,

(1) P. C. Myhre, C. D. Fisher, A. T. Nielsen, and W. M. Schubert, *J. Am. Chem. Soc.*, **87**, 29 (1965).

(2) E. R. Howells, D. C. Phillips, and D. Rogers, *Acta Cryst.*, **3**, 210 (1950).

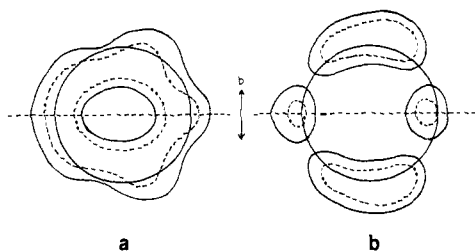


Figure 1. Difference synthesis showing the electron density in the plane of the *p*-methyl H atoms: circles are the traces of H atoms for methyl groups rotating about the bonds joining them to the rings; (a) C(25)H₃ and (b) C(20)H₃; solid contour at 0.25 electron Å⁻³, broken contour at 0.30 electron Å⁻³.

$R = \frac{\sum |F_o| - |F_c|}{\sum |F_o|}$, was 60.7%. This *R*, based on less than a quarter of the electrons in the structure, is to be compared with 83% which is expected for a centrosymmetric structure with all atoms included but in purely random positions.³

In the next set of structure factor calculations, the twelve C atoms of the two rings were included. These, together with the perchlorate group, account for 56% of the electrons in the adduct. After rescaling, *R* was 44.1%. Subsequent *F_c* syntheses were used to adjust the positions of the atoms already included and to locate the remaining nonhydrogen atoms. *R* now stood at 23.7%, and the atomic positions agreed closely with those derived from the Patterson synthesis. An additional refinement cycle based on a ΔF synthesis reduced *R* to 22.1%. The ΔF synthesis indicated no gross errors nor major electron density unaccounted for.

Least-Squares Refinement.⁴ A single full matrix least-squares refinement cycle with over-all temperature factor, followed by another in which individual atom thermal parameters as well as positional parameters were allowed to vary, reduced *R* to 16.9%. Two reflections (10 $\bar{1}$ and 111) with large discrepancies between *F_o* and *F_c* apparently suffered severe secondary extinction and were given zero weight in subsequent least-squares calculations. Two additional refinement cycles in which atomic positions, individual atom isotropic temperature factors, and scale factors were allowed to vary reduced *R* to 13.8%.

Isotropic temperature factors were converted next to anisotropic and refined in two additional least-squares cycles. After correcting a few obvious errors in the data, another refinement cycle in which only the scale factors and atomic positions were varied reduced *R* to 10.7%.

A ΔF synthesis at this point showed peaks at the 24 expected positions for the 24 H atoms bonded to carbon, although the six H atoms in the *p*-methyl groups could not be located as distinct entities. It was clearly evident that these methyl groups were rotating more or less freely about the bond joining the methyl groups to the rings (Figure 1a,b).⁵ For the sake of simplicity in calculating the structure factors, 12 quarter H atoms were distributed uniformly on the circle that

(3) A. J. C. Wilson, *Acta Cryst.*, **3**, 398 (1950).

(4) W. R. Busing and H. A. Levy, "A Crystallographic Least Squares Refinement Program for the IBM 704," U. S. Atomic Energy Commission Publication ORNL 59-4-37, 1959.

(5) Though less likely, it is possible that the methyl groups are fixed with the hydrogen atoms statistically distributed at random azimuth.

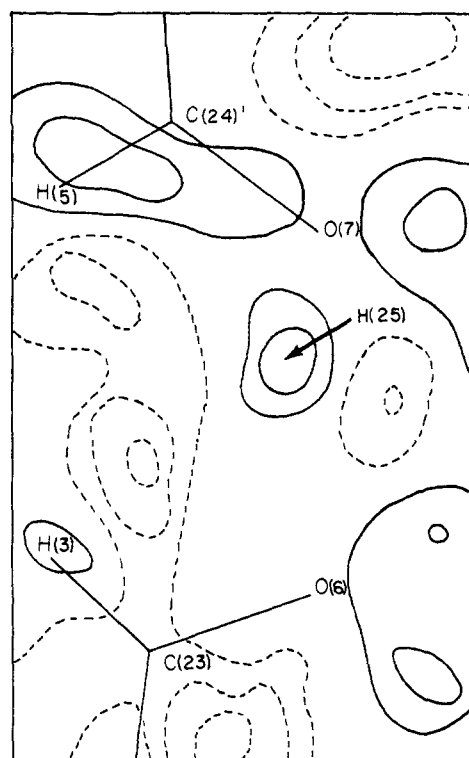


Figure 2. Difference synthesis showing the electron density in the region of the formyl groups: contour interval is 0.1 electron Å⁻³, positive contours solid, negative contours broken, zero contour omitted.

would be described by the H atoms of a freely rotating methyl group. These plus the additional 18 H atoms of the organic part of the adduct were included at their calculated positions⁶ in the next least-squares cycle. The electron of the remaining hydrogen was localized on the Cl atom by using the scattering factor for Cl⁻ in the structure factor calculations. The reliability index decreased to 8.9%.

The quality of the zero-level data was somewhat inferior to that of the other six levels. Accordingly, the zero-level data were redetermined and used in a subsequent refinement cycle in which only the atomic positions were varied, followed by another in which only the anisotropic thermal parameters were varied. Standard deviations improved appreciably, and the final *R* was 8.0%.

Further refinement of the structure is unwarranted in view of the limited data and the fact that it was uncorrected for absorption. Nevertheless, a ΔF synthesis (based on *F_c* values that included contributions from all atoms except the 25th hydrogen atom) was calculated in an attempt to locate the electron density associated with the proton from the perchloric acid. A peak lying between O(6) and O(7), Figure 2, while not definitive, is at least indicative of the location of the proton.

The final *F_o* synthesis is shown in Figure 3. Bond lengths and angles appear in Tables I and II. Final atomic parameters as well as the observed and calculated structure factors are available.⁷

(6) Carbon-hydrogen bond distances of 1.00 and 1.05 Å. were assumed for trigonal and tetragonal bonds, respectively.

(7) Microfilms of these data can be obtained for \$1.75 from the ADI Auxiliary Publications Project, Library of Congress, Washington 25, D. C., Document No. 8099.

Table I. Bond Lengths of Covalent Bonds Not Involving Hydrogen Atoms and Their Estimated Standard Deviations

Bond	Length, Å.	Bond	Length, Å.
Cl(1)-O(2)	1.419 ± 0.011	C(12)-C(13)	1.426 ± 0.015
Cl(1)-O(3)	1.431 ± 0.012	C(12)-C(23)	1.443 ± 0.015
Cl(1)-O(4)	1.418 ± 0.008	C(13)-C(22)	1.493 ± 0.016
Cl(1)-O(5)	1.418 ± 0.008	C(14)-C(15)	1.371 ± 0.014
O(6)-C(23)	1.252 ± 0.013	C(14)-C(19)	1.384 ± 0.015
O(7)-C(24)	1.249 ± 0.012	C(15)-C(16)	1.449 ± 0.013
C(8)-C(9)	1.400 ± 0.015	C(15)-C(27)	1.510 ± 0.013
C(8)-C(13)	1.398 ± 0.014	C(16)-C(17)	1.388 ± 0.014
C(9)-C(10)	1.375 ± 0.015	C(16)-C(24)	1.406 ± 0.013
C(9)-C(20)	1.514 ± 0.016	C(17)-C(18)	1.385 ± 0.015
C(10)-C(11)	1.409 ± 0.015	C(17)-C(26)	1.545 ± 0.016
C(11)-C(12)	1.403 ± 0.015	C(18)-C(19)	1.401 ± 0.015
C(11)-C(21)	1.507 ± 0.015	C(19)-C(25)	1.524 ± 0.018

Table II. Bond Angles for Covalent Bonds Not Involving Hydrogen Atoms and Their Estimated Standard Deviations

Angle	Degrees
O(2)-Cl(1)-O(3)	108.7 ± 0.6
O(2)-Cl(1)-O(4)	109.0 ± 0.6
O(3)-Cl(1)-O(4)	111.8 ± 0.6
O(4)-Cl(1)-O(5)	106.4 ± 0.8
O(6)-C(23)-C(12)	126.0 ± 0.7
O(7)-C(24)-C(16)	127.9 ± 0.6
C(8)-C(9)-C(10)	120.8 ± 0.8
C(8)-C(9)-C(20)	118.4 ± 0.8
C(8)-C(13)-C(12)	117.9 ± 0.7
C(8)-C(13)-C(22)	118.2 ± 0.8
C(9)-C(8)-C(13)	120.3 ± 0.7
C(9)-C(10)-C(11)	121.5 ± 0.8
C(10)-C(9)-C(20)	120.5 ± 0.8
C(10)-C(11)-C(12)	117.3 ± 0.7
C(10)-C(11)-C(21)	117.0 ± 0.8
C(11)-C(12)-C(13)	122.2 ± 0.7
C(11)-C(12)-C(23)	122.4 ± 0.7
C(12)-C(11)-C(21)	125.7 ± 0.7
C(12)-C(13)-C(22)	123.9 ± 0.7
C(13)-C(12)-C(23)	115.4 ± 0.7
C(14)-C(15)-C(16)	117.6 ± 0.7
C(14)-C(15)-C(27)	118.3 ± 0.7
C(14)-C(19)-C(18)	118.4 ± 0.8
C(14)-C(19)-C(25)	122.2 ± 0.8
C(15)-C(14)-C(19)	123.3 ± 0.7
C(15)-C(16)-C(17)	119.4 ± 0.7
C(15)-C(16)-C(24)	120.8 ± 0.7
C(16)-C(15)-C(27)	124.1 ± 0.6
C(16)-C(17)-C(18)	120.6 ± 0.7
C(16)-C(17)-C(26)	121.1 ± 0.8
C(17)-C(16)-C(24)	119.7 ± 0.7
C(17)-C(18)-C(19)	120.6 ± 0.7
C(18)-C(17)-C(26)	118.3 ± 0.8
C(18)-C(19)-C(25)	119.3 ± 0.8

Scattering factors used were those of Berghuis, *et al.*, for carbon and oxygen,⁸ of McWeeny for hydrogen,⁹ and of Dawson for the chloride ion.¹⁰

Results and Discussion

A projection of the non-H atoms of the 2:1 mesitaldehyde-perchloric acid adduct along the *b*-axis of the unit cell is shown in Figure 4. There are several notable features of the crystal structure. All of the mesitaldehyde moieties are in planes parallel to (010) and separated by $b/2 = 3.46$ Å. However, they are packed together in two different ways. Half of them have the

(8) J. Berghuis, I. M. Haanappel, M. Potters, B. O. Loopstra, C. H. MacGillavry, and A. L. Veenendaal, *Acta Cryst.*, **8**, 478 (1955).

(9) R. McWeeny, *ibid.*, **4**, 513 (1951).

(10) B. Dawson, *ibid.*, **13**, 403 (1960).

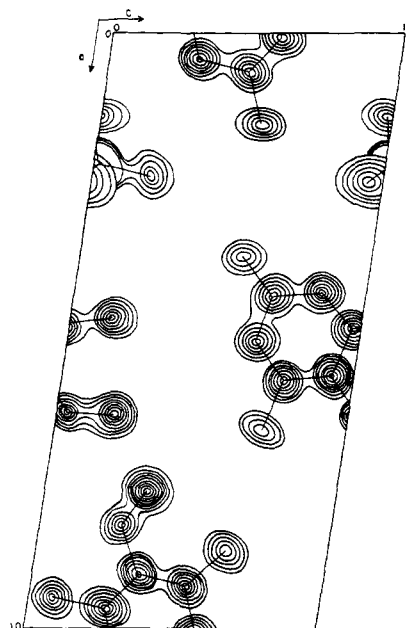


Figure 3. Composite F_0 synthesis for mesitaldehyde-perchloric acid 2:1 adduct showing electron density: contour interval 1.0 electron Å.⁻³, chlorine atom not contoured above 3 electrons Å.⁻³, and hydrogen atoms not shown.

rings partly overlapping, with the coplanar formyl substituents lying 180° from each other (see A and A' in Figure 4). The other half have no ring overlap. Instead, an *o*-methyl group in one layer overlaps the approximate center of a ring in the layer above and below (B and B' in Figure 4). Moieties of type A and B are so arranged with respect to each other as to allow hydrogen bridging between them, *i.e.*, between O(6) and O(7).

The Hydrogen Bond. Although H(25) was not clearly located, it must lie between the carbonyl O atoms of A and B type moieties. The O(6)-O(7) distance, 2.46 ± 0.01 Å., is much less than the sum of the van der Waals radii and, in fact, indicates a very strong O---H---O bridge. The O(6)-O(7) distance is comparable to the very short O-O distances reported for nickel dimethylglyoxime (2.44 Å.),¹¹ potassium hydrogen maleate (2.437 Å.),¹² ammonium hydrogen disalicylate hydrate (2.45 Å.),¹³ and acetamide hydrochloride (2.40 Å.).¹⁴

The question arises as to whether the bridging hydrogen lies in a single or a double potential energy minimum. A somewhat scattered plot given by Pimentel and McClellan predicts the merging into a single minimum only at O-O distances appreciably shorter, *ca.* 2.30 Å., than the one found here.¹⁵

If there are two potential energy minima for the bridging hydrogen atom, the O(6)-O(7) distance is probably sufficiently short for the barrier between them to be low.¹⁶ One of the potential energy minima for the *entire crystal* could correspond to half of the

(11) L. E. Godycki and R. E. Rundle, *ibid.*, **6**, 487 (1953).

(12) S. F. Darlow and W. Cochran, *ibid.*, **14**, 1250 (1960).

(13) T. C. Downie and J. C. Speakman, *J. Chem. Soc.*, 787 (1954).

(14) W. J. Takei and E. W. Hughes, and E. W. Peterson and H. Levy, as reported by L. Pauling, "The Nature of the Chemical Bond," 3rd Ed., Cornell University Press, Ithaca, N. Y., 1960, p. 485.

(15) G. C. Pimentel and A. L. McClellan, "The Hydrogen Bond," W. H. Freeman and Co., San Francisco, Calif., 1960, p. 259.

(16) Reference 15, p. 261.

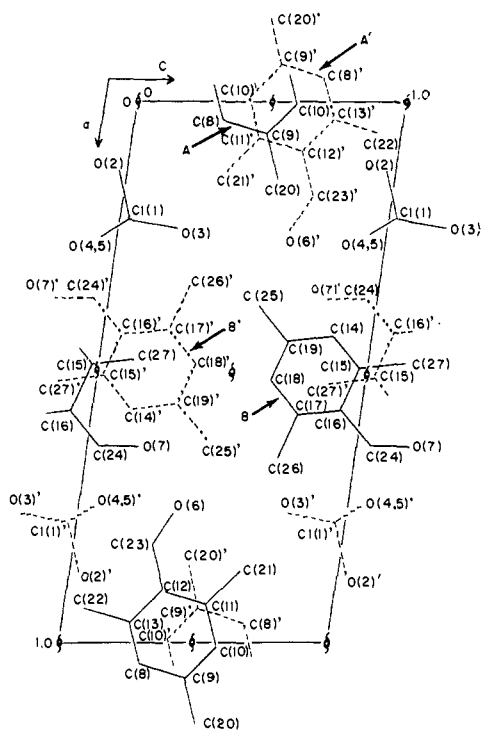


Figure 4. Projection of unit cell along b . Atoms at $y = 1/4$ joined by solid lines; those at $y = 3/4$ joined by broken lines.

bridging hydrogens being closer to A moieties in *alternate* layers, the other half being closer to B moieties in the other layers. In the other potential energy minimum, the proton positions would be just reversed.¹⁷ The two states of the crystal as a whole would have the same energy. However, the time average position of a bridging hydrogen should be somewhat off-center since A and B mesitaldehyde moieties are in different environments. In either potential energy minimum, A (or B) moieties having positive sites would be stacked alternately above and below relatively electron-rich A (or B) moieties. A net attractive force between molecular layers could result, and this is consistent with the close packing of the layers.

An attractive force between molecular layers also could arise should the hydrogen lie in a nearly centrally located single minimum. Adjoining A and B moieties and the bridging hydrogen would in effect constitute a single entity, with resonance distribution of the single positive charge among the three parts making up the entity. The electron motions in the layers could be synchronized; *i.e.*, at the instant when certain sites of an A (or B) carry maximum positive character, the A (or B) above and below could be relatively electron rich, and net attraction between layers could result.

The bridging hydrogen would be expected to have considerable positive character, *i.e.*, low electron density. It is therefore not surprising that this hydrogen is the only one not clearly located. There was a possible indication of a bit of electron density between O(6) and O(7) as shown in Figure 2. If the peak between O(6) and O(7) found at 0.97 Å. from O(7) is assumed to be an H atom, then its position does not differ significantly from the midpoint of a line joining

(17) In neighboring stacks of A (or B) moieties, the proton positions in a particular layer could be either: (1) close to A in one stack, close to B in the other; or (2) both protons close to A or both close to B.

O(6) and O(7). While the standard deviations in positions of the H atoms were not determined, values 10–12 times those for C atoms are expected on the basis of other work. For 2:1 mesitaldehyde-perchloric acid adduct, the standard deviation in position for a H atom would be about 0.12 Å. By the usual crystallographic significance criteria,¹⁸ the true position of an atom should not differ from that found by more than 2.6 σ .

The situation for 2:1 mesitaldehyde-perchloric acid adduct is reminiscent of that reported by Takei and Hughes, and Peterson and Levy for acetamide hemihydrochloride.¹⁴ In that adduct, the O–O distance is 2.40 ± 0.02 Å., and the bridging hydrogen is tentatively located as being either in a single minimum midway between the oxygen atoms or in double minima a short distance on either side of the midpoint.^{14, 19} The reported C–O bond length,¹⁴ 1.244 ± 0.012 Å., corresponds closely to the values found in this work, 1.249 ± 0.012 and 1.252 ± 0.013 Å. (uncorrected for rotational oscillations), for O(7)–C(24) and O(6)–C(23), respectively.

Packing of Type A Moieties. The rings of the mesitaldehyde moieties of type A and A', in which there is ring overlap in adjoining layers, are one-half unit cell apart, 3.46 Å. This is close to the intermolecular distance reported for 1:14-benzbisanthrene (3.40 Å.),²⁰ 1:12-benzperylene (3.38 Å.),²¹ coronene (3.40 Å.),²² and similar polynuclear aromatics. Most aromatic compounds have interplanar distances greater than 3.50 Å. Interplanar distances from 3.16 to 3.50 Å. have been observed for molecular complexes of aromatic compounds. The distance between hydroquinone and quinone moieties in quinhydrone is 3.16 Å.,²³ while the interplanar distance between alternating layers of *p*-iodoaniline and 1,3,5-trinitrobenzene in the 1:1 adduct of these compounds is about 3.50 Å.²⁴ The fact that the A moieties in 2:1 mesitaldehyde-perchloric acid adduct are closely packed may indicate an appreciable attractive force between them. Since the rings partly overlap, this attraction could be considered to be of a π -complex nature.²⁵

The distortions of some of the bond angles in the A moieties could be in part a reflection of the close packing. Angles C(11)–C(12)–C(23) and especially C(12)–C(11)–C(21) and O(6)–C(23)–C(12) are larger than normal trigonal bond angles. This may be because the formyl group and the C(21) *o*-methyl are bent back somewhat in order to accommodate the *p*-methyl groups, C(20)', in adjacent molecular planes (Figure 4). As a result, the formyl group may, in turn, be bearing against the C(22) *o*-methyl, increasing the C(12)–C(13)–C(22) angle to $123.9 \pm 0.7^\circ$. On the other hand, these angle distortions may be caused largely by repulsion between O(6) and the C(21) methyl.

(18) D. W. J. Cruickshank and A. P. Robertson, *Acta Cryst.*, **6**, 698 (1953).

(19) E. W. Peterson, personal communication.

(20) J. Trotter, *Acta Cryst.*, **11**, 423 (1958).

(21) J. G. White, *J. Chem. Soc.*, 1398 (1948).

(22) J. M. Robertson and J. G. White, *ibid.*, 607 (1945).

(23) H. Matsuda, K. Osaki, and I. Nitta, *Bull. Chem. Soc., Japan*, **31**, 611 (1958).

(24) H. M. Powell, G. Huse, and P. W. Cooke, *J. Chem. Soc.*, 153 (1943).

(25) S. C. Wallwork, *ibid.*, 494 (1961).

Packing of Type B Moieties. An intriguing feature of the packing of the B-type moieties is that the ring overlap featured by the A moieties is absent. Instead there is overlap of the C(27) *o*-methyl substituent of one B-type moiety with the rings of the B moieties immediately above and below (Figure 4). Furthermore, from the ΔF map, it is evident that the overlapping methyl is not free to rotate. One of the hydrogen atoms of the *o*-methyl is in the molecular plane. The other two are above and below the molecular plane, packed tightly nearly into the centers of the benzene rings of the adjacent layers. Each of these two methyl H atoms is located 2.60 Å. from the ring C atoms (Table III). The distance from the center of the H atom to the plane of the ring is about 0.3 Å. less than the sum of the normal van der Waals radius for hydrogen, 1.20 Å., plus that given for an aromatic molecule, 1.70 Å.²⁶ Thus two of the methyl H atoms appear to penetrate into the dimples in the centers of the π -electron clouds of the sandwiching rings.

Table III. Some Intermolecular Distances

Bond	Length, Å.
O(6)-O(7)	2.459 ± 0.010
H(C27)'-C(14)	2.88
H(C27)'-C(15)	2.96
H(C27)'-C(16)	3.02
H(C27)'-C(17)	3.02
H(C27)'-C(18)	2.95
H(C27)'-C(19)	2.89

The molecular distortions necessary to accommodate the close packing of *o*-methyl groups and rings of B moieties in alternate layers may account for the elongated C(15)-C(16) bond (1.449 ± 0.013 Å.), the larger than normal C(15)-C(14)-C(19) angle (123.3 ± 0.7°), and the larger than normal C(16)-C(15)-C(27) angle (124.1 ± 0.6°). The bond angles at the trigonal C(16) are all close to 120°. This would appear to suggest that the bond angle distortions in A moieties at C(12) are due to interlayer crowding by the C(20)' methyls.

Exocyclic Bonds. The exocyclic C(12)-C(23) and C(16)-C(24) bonds are unusually short having lengths 1.443 ± 0.015 and 1.406 ± 0.013 Å. as compared to a normal sp²-sp² bond length of 1.479 Å.^{27,28} This could be attributed to a large amount of double-bond character caused by the presence of the extra proton.

The exocyclic carbon-carbon bonds in benzamide, benzoic acid, and salicylic acid have lengths of 1.48,²⁹ 1.48,³⁰ and 1.46 Å.,³¹ respectively.

The sp²-sp³ carbon-carbon bonds of the methyl substituents are probably not significantly different from the value of 1.51 Å. found for toluene.³²

(26) L. Pauling, ref. 14, p. 260.

(27) M. J. S. Dewar and H. N. Schmeising, *Tetrahedron*, **5**, 166 (1959).

(28) R. S. Mulliken, *ibid.*, **6**, 68 (1959).

(29) B. R. Penfold and J. C. B. White, *Acta Cryst.*, **12**, 130 (1959).

(30) G. A. Sim, J. M. Robertson, and T. H. Goodwin, *ibid.*, **8**, 157 (1955).

(31) W. Cochran, *ibid.*, **6**, 260 (1953).

(32) F. A. Keidel and S. H. Bauer, *J. Chem. Phys.*, **25**, 1218 (1956).

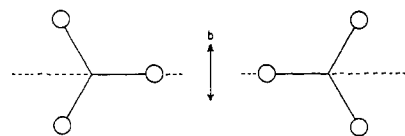


Figure 5. Main conformations of methyl group C(20)H₃.

Methyl Substituents. Distinct areas of electron density are found on the ΔF map for each of the *o*-methyl H atoms. Crowding of the formyl groups between the *o*-methyl substituents apparently hinders rotation of these methyl groups. As has been pointed out above, the C(27) methyl group is further restricted by close interlayer packing. Formyl H and O atoms are just at van der Waals distances from the methyl H atoms which straddle them.

The ΔF map in a section through the expected position of the methyl H atoms on C(25) (Figure 1a) may be explained by assuming essentially free rotation about the C(19)-C(25) bond. The corresponding ΔF section showing the methyl H atoms on C(20) (Figure 1b) indicates hindered rotation (or disorder) in which the predominant conformations are those shown in Figure 5.

Perchlorate Ion. The Cl-O bonds of the perchlorate ion in 2:1 mesitaldehyde-perchloric acid adduct do not differ significantly from each other. When corrected for rotational oscillation,³³ the bond lengths become 1.456 ± 0.012, 1.486 ± 0.013, and 1.456 ± 0.009 Å. for bonds Cl(1)-O(2), Cl(1)-O(3), and Cl(1)-O(4), respectively. The weighted mean Cl-O bond length of 1.458 ± 0.007 Å. is in excellent agreement with recently reported values for several other perchlorate salts.³⁴⁻³⁷

The O(4) and O(5) atoms of the perchlorate ion are out of hydrogen bonding range with respect to any reasonably placed bridging hydrogen between O(6) and O(7) of the layers above and below. The distance from either O(4) or O(5) to the O(6)-O(7) line is 3.18 Å. The observed distance from O(4) or O(5) to the formyl H atom (at its calculated position) is 2.56 Å., whereas the sum of the oxygen radius, 1.40 Å., and the hydrogen radius, 1.20 Å., is 2.60 Å.²⁶ There might be a concomitant constraint of the O(4)-Cl(1)-O(5) angle to a smaller value than the O(2)-Cl(1)-O(3) angle, especially since the van der Waals radii of the somewhat negative oxygens of perchlorate ion may be greater than normal. The value found for the O(4)-Cl(1)-O(5) angle (106.4 ± 0.8°) is indeed smaller than that found for the O(2)-Cl(1)-O(3) angle (108.7 ± 0.6°), although the difference is only possibly significant.

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