The crystal structure of twinned $Cd_5(PO_4)_3Cl$, 'cadmium chlorapatite': erratum.

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The bond angles and interatomic distances listed in the original paper [Sudarsanan, Young & Donnay (1973). *Acta Cryst.* B29, 808–814] were inadvertently taken from calculations based on a set of temporarily used values of the lattice parameters. The correct values, based on the final lattice-parameter values included in the paper, are given. The largest correction thus made to any distance is 0·3 %, *e.g.*, 0·010 Å in the $Cd_{II}-O_I$ distance.

The correct values of the bond angles and interatomic distances listed in Table 4 of the original paper are as follows:

(*a*) Bond angles and their standard deviations

O_I-P-O_{III}	112·6 (0·1)°
O_I-P-O_{II}	110·7 (0·1)
$O_{II}-P-O_{III}$	107·1 (0·1)
$O_{III}-P-O'_{III}$	106·4 (0·1)

(*b*) Interatomic distances and their standard deviations

O_I-P	1·525 (1) Å
$O_{II}-P$	1·557 (1)
$O_{III}-P$	1·540 (1)
O_I-O_{II}	2·536 (2)
$O_{II}-O_{III}$	2·490 (2)
O_I-O_{III}	2·550 (2)
$O_{III}-O'_{III}$	2·467 (2)

Cd_I-O_I	2·310 (1)
Cd_I-O_{II}	2·376 (1)
Cd_I-O_{III}	2·871 (2)
$Cd_{II}-O_I$	3·148 (2)
$Cd_{II}-O_{III}$	2·202 (1)
$Cd_{II}-O_{III}$	2·460 (1)
$Cd_{II}-O_{II}$	2·246 (2)
$Cd_{II}-Cl$	2·537 (1)

Reference

SUDARSANAN, K., YOUNG, R. A. & DONNAY, J. D. H. (1973). *Acta Cryst.* B29, 808–814.

The crystal structures of tropolone and 4-isopropyltropolone: a comparison.

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Comparison of bond lengths determined by X-ray crystal structure analyses indicates that the degree of π-electron delocalization is smaller in 4-isopropyltropolone than in tropolone, but in both molecules it is greater than that predicted by SCF MO calculations.

In a recent paper on the crystal structure of 4-isopropyltropolone (IPT) (Derry & Hamor, 1972), it was noted that the bond lengths did not agree with those observed in the crystal structure of tropolone by Shimanouchi & Sasada (1970), where, apart from a long C(1)–C(2) bond of 1·452 Å, ring bond lengths (mean 1·407 Å) are close to the aromatic value and there is no alternation in length. IPT, in contrast, exhibits bond-length alternation in the sense predicted by the classical valence bond structure, with the C(1)–C(2) length 1·469 Å, close to the $C(sp^2)-C(sp^2)$ single-bond value. The other C–C formal single bonds average 1·416 Å and the double bonds 1·362 Å, respectively shorter and longer than pure single and double bonds, so that the π-electron system is partially delocalized. The carbon-oxygen bonds are also involved in the electron delocalization as indicated by the lengths, C(1)–O(1) = 1·261 and C(2)–O(2) = 1·349 Å. A revised report on the tropolone structure, based on re-measured intensities, has now appeared (Shimanouchi & Sasada, 1973). This indicates that there is in fact bond-length alternation in the ring, in agreement with the situation in IPT. Bond lengths from these three studies are listed in Table 1, with the results of a MO treatment of tropolone (Dewar semi-empirical SCF & Trinajstic, 1970).
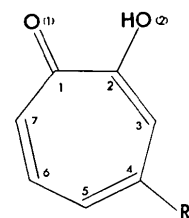
4-Isopropyltropolone $R = CHMe_2$
Tropolone $R = H$

Generally, the revised bond lengths for tropolone agree fairly well with those in IPT. A closer examination, however, reveals certain differences which follow a systematic trend. The C(1)–C(2) bond in tropolone is shorter by 0·015 Å than the corresponding bond in IPT and the other formal C–C single bonds average 1·404 Å, shorter by 0·012 Å than the average in IPT. The double bonds average 1·364 Å, very slightly longer than the average in IPT (1·362 Å). The indication, therefore, is that the π-electron system is delocalized to a slightly smaller extent in IPT than in tropolone. Consistent with this, the C(2)–O(2) bond length is shorter by 0·016 Å in tropolone. The C(1)–O(1) lengths are, how-

Table 1. *Comparison of bond lengths* (Å)

	Tropolone*	IPT†	Tropolone‡	Tropolone§
C(1)–O(1)	1·268 (8)	1·261 (5)	1·261 (3)	1·258
C(2)–O(2)	1·329 (8)	1·349 (5)	1·333 (3)	1·389
C(1)–C(2)	1·452 (8)	1·469 (6)	1·454 (4)	1·462
C(3)–C(4)	1·406 (8)	1·422 (6)	1·393 (4)	1·452
C(5)–C(6)	1·433 (8)	1·413 (6)	1·410 (4)	1·452
C(7)–C(1)	1·424 (8)	1·413 (7)	1·410 (3)	1·462
Mean single bonds [excluding C(1)–C(2)]	1·421	1·416	1·404	1·455
C(2)–C(3)	1·428 (8)	1·367 (5)	1·379 (4)	1·355
C(4)–C(5)	1·346 (8)	1·355 (6)	1·341 (4)	1·357
C(6)–C(7)	1·405 (8)	1·364 (6)	1·373 (4)	1·355
Mean double bonds	1·393	1·362	1·364	1·356
Mean double bonds [excluding C(4)–C(5)]	1·416	1·365	1·376	1·355

* Shimanouchi & Sasada, 1970 (X-ray).
† Derry & Hamor, 1972 (X-ray).
‡ Shimanouchi & Sasada, 1973 (X-ray).
§ Dewar & Trinajstic, 1970 (SCF MO calculation).

ever, the same, although this bond might have been expected to be slightly longer in tropolone than in IPT.

In both molecules the C(4)–C(5) formal double bond is shorter than the other two C–C double bonds. The difference is much more marked in tropolone, where this bond has a length of only 1·341 Å, close to the accepted value for a pure double bond (1·335 Å). Interestingly, the SCF MO calculations lead to a length of 1·357 Å for this bond, slightly longer than the other carbon–carbon double bonds. If this bond is omitted from the averaging, then the mean double bond length in tropolone is 1·376 Å.

The seven-membered rings of both tropolone and IPT deviate slightly, and in a similar way, from planarity, the root mean square deviations of the atoms from the least-squares plane being 0·015 Å in tropolone and 0·018 Å in IPT. Shimanouchi & Sasada (1973) noted that the ring in tropolone adopts a boat conformation similar to, but shallower than, that observed for a number of tropones. In the tropones, the 'boat' is described in terms of the planes defined by the three groups of atoms C(1,2,7), C(2,3,6,7) and C(3,4,5,6), and these same groups of atoms were used to describe the boat conformation of the tropolone ring, the r.m.s. atomic deviations being 0, 0·009 and 0·007 Å, respectively. However, a better description of the ring conformation, also in terms of a 'boat', makes use of the three planes defined by the atoms C(1,2,3,7), C(3,4,6,7) and C(4,5,6). The r.m.s. atomic deviations for the four-atom planes are now smaller, 0·006 and 0·001 Å. In IPT the r.m.s. deviations are 0·002 and 0·001 Å. The interplanar angles C(1,2,3,7) ∧ C(3,4,6,7) and C(4,5,6) ∧ C(3,4,6,7) are 2·1 and 1·8° in tropolone, and 2·6 and 2·2° in IPT. The slightly greater degree of non-planarity of the ring in IPT is consistent with the smaller degree of π-electron delocalization in this molecule indicated by the comparison of bond lengths. The fact that the tropolone ring conformation appears to differ from the tropone ring conformation in the manner indicated above may be a consequence of the greater degree of electron delocalization in tropolones as compared with tropones (Derry & Hamor, 1972; Shimanouchi & Sasada, 1973), and of the partial double-bond character of the C(2)–O(2) bond.

The SCF MO calculations predict almost identical bond lengths for tropone and tropolone, with single bonds averag-

ing 1·457 Å and double bonds 1·356 Å, and no distinction between the C(1)–C(2) and C(1)–C(7) bonds. These results are in reasonable agreement with X-ray crystallographic results for tropones, but indicate a more marked degree of bond alternation for tropolone than is observed in the crystal structures of IPT or tropolone.

In the crystal structures of both IPT and tropolone, the hydroxyl group is involved in hydrogen bonding with the ketonic oxygen atom. In the tropolone structure this is a bifurcated bond, the ketonic oxygen atoms of both the same and one neighbouring molecule participating. In IPT the hydroxylic hydrogen atom could not be located, but it was considered that there was an intermolecular H-bond with the O(2)···O(1)′ distance 2·80 Å. The packing arrangement is, however, not favourable for the type of bonding observed in tropolone involving both intra- and intermolecular interactions. In the intermolecular branch of the bifurcated H-bond of tropolone the O(2)···O(1)′ distance is 2·754 Å indicating a stronger interaction than in the IPT structure.

Shinanouchi & Sasada (1973) have emphasized the importance of H-bonding in promoting π-electron delocalization in the tropolone system. The difference in the strengths of the H-bonding may therefore account for the slightly smaller degree of electron delocalization in IPT. The electron-releasing properties of the isopropyl group in IPT would, however, also be a contributory factor in this, and it does not seem possible to assess the relative importance of these effects.

The SCF MO calculations take neither intra- nor intermolecular hydrogen bonding into consideration and are therefore not directly comparable with the X-ray crystallographic studies on tropolone and IPT.

References

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