Crystal and Molecular Structure of 4-Isopropyltropolone (β-Thujaplicin)

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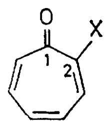
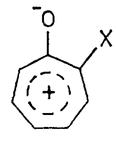
The π-electron system in 4-isopropyltropolone (IV) has been shown by *X*-ray crystallographic analysis, by use of three-dimensional counter data, to be partially delocalised. Within the ring, the C(1)–C(2) bond remains essentially a single bond (1·469 Å), and the means of the other formal single and double C–C bonds are 1·416 and 1·362 Å. The atoms of the ring deviate slightly, but significantly, from coplanarity. The crystals are monoclinic, space group *I*2/*c* with *Z* = 8 in a cell of dimensions: *a* = 17·063, *b* = 6·469, *c* = 15·970 Å, and β = 90·77°. The structure was solved by the symbolic addition procedure and refined by least squares methods to a final *R* of 8·3% for 1272 structure amplitudes.

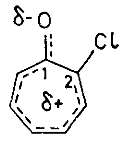
TROPONE (I; X = H) and tropolone (I; X = OH) have both been classified [1,2] as non-benzenoid aromatic compounds owing to a presumed ground-state contribution from the cyclically delocalised six π-electron resonance structure (II). It has been pointed out,[1] however, that the chemical properties of tropone can be explained without recourse to any particular aromatic character, and *X*-ray analysis [3] of 2-chlorotropone (I; X = Cl) is in agreement with this conclusion. The results of the analysis show that the molecule may best be depicted by the non-cyclically partially delocalised structure (III) with the C(1)–C(2) bond essentially a C(sp^2)–C(sp^2) single bond of length 1·49 Å. However, differing views have been expressed concerning the aromatic character of tropolone (*cf.* refs. 1 and 2). Recently Bertelli and co-workers [4] have concluded, on the basis of dipole moment and n.m.r. measurements and CNDO/2 MO calculations, that neither tropone nor tropolone possess any appreciable degree of aromatic character.



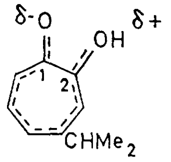
(I)



(II)



(III)



(IV)

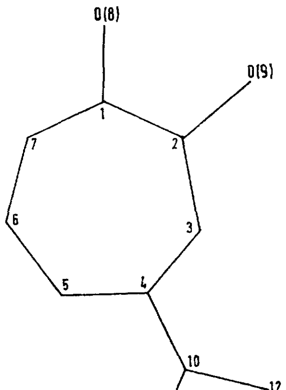


FIGURE 1 The numbering system used in the analysis

X-Ray analysis of tropolone,[5] based on visually estimated intensity data, indicates that the C(1)–C(2) bond length is 1·452 Å with the other ring bonds close to the standard aromatic value (1·394 Å),[6] so that at least partial cyclic π-electron delocalisation apparently occurs.

TABLE 1

Atomic co-ordinates (× 10^4) with estimated standard deviations in parentheses

	x/*a*	*y*/*b*	*z*/*c*
C(1)	3074(2)	3103(7)	4064(2)
C(2)	2998(2)	4782(6)	3449(2)
C(3)	3251(2)	4894(6)	2642(2)
C(4)	3691(2)	3476(7)	2155(2)
C(5)	3948(3)	1594(7)	2410(3)
C(6)	3823(3)	579(7)	3180(3)
C(7)	3445(3)	1205(8)	3883(3)
O(8)	2770(2)	3432(5)	4767(2)
O(9)	2599(2)	6433(5)	3733(2)
C(10)	3880(3)	4306(8)	1290(2)
C(11)	4481(4)	6044(11)	1347(4)
C(12)	4155(4)	2694(10)	663(3)
H[C(3)]	3046(22)	6227(65)	2402(24)
H[C(5)]	4240(24)	783(69)	1980(27)
H[C(6)]	4097(25)	−852(73)	3230(26)
H[C(7)]	3440(25)	171(73)	4371(27)
H[C(10)]	3360(24)	4904(71)	1045(24)
H^1[C(11)]	5039(31)	5512(82)	1572(31)
H^2[C(11)]	4524(31)	6600(83)	794(34)
H^3[C(11)]	4396(30)	7157(84)	1805(33)
H^1[C(12)]	4146(29)	3271(77)	87(31)
H^2[C(12)]	3830(30)	1439(79)	601(30)
H^3[C(12)]	4702(30)	2042(78)	825(29)

Atomic parameters and molecular dimensions for the naturally occurring 4-isopropyltropolone (β-thujaplicin) based on three-dimensional counter data are listed in Tables 1—4. The numbering system used is shown in Figure 1. For lengths and angles not involving hydrogen atoms standard deviations are *ca.* 0·006 Å and 0·4°, respectively. Thermal parameters could not be readily interpreted in terms of rigid-body libration and no corrections for this effect have been made.

In contrast to the lengths measured for tropolone, the bonds in 4-isopropyltropolone alternate in length in the

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[1] D. M. G. Lloyd, 'Carbocyclic Non-Benzenoid Aromatic Compounds,' Elsevier, Amsterdam, 1966.

[2] G. M. Badger, 'Aromatic Character and Aromaticity,' Cambridge University Press, Cambridge, 1969.

[3] D. J. Watkin and T. A. Hamor, *J. Chem. Soc.* (*B*), 1971, 2167.

[4] D. J. Bertelli and T. G. Andrews, jun., *J. Amer. Chem. Soc.*, 1969, **91**, 5280; D. J. Bertelli, T. G. Andrews, jun., and P. O. Crews, *ibid.*, p. 5286.

[5] H. Shimanouchi and Y. Sasada, *Tetrahedron Letters*, 1970, 2421.

[6] *Chem. Soc., Special Publ.*, No. 18, 1965.

sense predicted by the classical structure (I), with the isopropyl group in the 4-position. The π-electron system is, however, partially delocalised. The formal double bonds in the ring, C(2)–C(3), C(4)–C(5), and C(6)–C(7) have lengths of 1·367, 1·355, and 1·364 Å, compared to 1·335 Å for the pure double-bond length,[6] while the formal single bonds C(3)–C(4), C(5)–C(6), and C(7)–C(1) of lengths 1·422, 1·413, and 1·413 Å are shorter than the accepted value for the length of the C(sp^2)–C(sp^2) single-bond (1·48—1·50 Å).[7,8] The C(1)–C(2) bond (1·469 Å) is significantly longer than the other carbon–carbon bonds and does not differ significantly from the single-bond value. The C–O bonds, C(1)–O(8) and C(2)–O(9) have lengths of 1·261 and 1·349 Å consistent with structure (I). These lengths differ significantly from the carbon–oxygen double-bond length [6] of 1·215 Å and the C(sp^2)–O single bond which we estimate to be *ca.* 0·03 Å shorter than the C(sp^3)–O single-bond length [6] of 1·43 Å (values for this bond are 1·402 Å in acetylsalicylic acid [9] and 1·410 Å in potassium L-tyrosine *O*-sulphate dihydrate [10]). It may therefore be concluded that the C–O bonds are included in the partial π-electron delocalisation.

TABLE 2

Anisotropic thermal parameters (× 10⁴) * for the heavier atoms

	U_{11}	U_{22}	U_{33}	$2U_{12}$	$2U_{13}$	$2U_{23}$
C(1)	574	504	417	−140	14	118
C(2)	550	445	399	14	80	10
C(3)	557	473	418	48	88	62
C(4)	429	540	417	−82	124	−52
C(5)	529	588	551	106	266	−54
C(6)	659	470	649	234	228	64
C(7)	730	538	539	42	42	264
O(8)	853	630	399	−100	274	52
O(9)	844	528	485	258	406	22
C(10)	599	737	396	80	208	54
C(11)	1133	868	548	−510	534	120
C(12)	826	880	518	90	216	−330

* Temperature factors are in the form:

$$T = \exp[-2\pi^2(U_{11}h^2a^{*2} + \cdots + 2U_{12}hka^*b^* + \cdots)].$$

TABLE 3

Molecular dimensions

(*a*) Bond lengths (Å) with standard deviations (× 10³) in parentheses

C(1)–C(2)	1·469(6)	C(3)–H[C(3)]	1·00
C(2)–C(3)	1·367(5)	C(5)–H[C(5)]	1·00
C(3)–C(4)	1·422(6)	C(6)–H[C(6)]	1·04
C(4)–C(5)	1·355(6)	C(7)–H[C(7)]	1·03
C(5)–C(6)	1·413(6)	C(10)–H[C(10)]	1·04
C(6)–C(7)	1·364(6)	C(11)–H^1[C(11)]	1·07
C(7)–C(1)	1·413(7)	C(11)–H^2[C(11)]	0·96
C(1)–O(8)	1·261(5)	C(11)–H^3[C(11)]	1·04
C(2)–O(9)	1·349(5)	C(12)–H^1[C(12)]	0·99
C(4)–C(10)	1·522(5)	C(12)–H^2[C(12)]	0·99
C(10)–C(11)	1·523(8)	C(12)–H^3[C(12)]	1·05
C(10)–C(12)	1·525(7)		

(*b*) Bond angles (deg.). Mean standard deviation for angles not involving hydrogen atoms is 0·4°

C(7)–C(1)–C(2)	122·8	H–C(6)–C(5)	114
O(8)–C(1)–C(7)	121·3	H–C(6)–C(7)	115
C(2)–C(1)–O(8)	115·9	H–C(7)–C(6)	116
C(1)–C(2)–C(3)	130·0	H–C(7)–C(1)	114
O(9)–C(2)–C(1)	113·6	H–C(10)–C(4)	106
C(3)–C(2)–O(9)	116·3	H–C(10)–C(11)	109
C(2)–C(3)–C(4)	131·0	H–C(10)–C(12)	106
C(3)–C(4)–C(5)	126·0	H^1–C(11)–C(10)	112
C(3)–C(4)–C(10)	112·8	H^2–C(11)–C(10)	106
C(5)–C(4)–C(10)	121·2	H^3–C(11)–C(10)	117
C(4)–C(5)–C(6)	128·8	H^1–C(11)–H^2	110
C(5)–C(6)–C(7)	131·1	H^1–C(11)–H^3	97
C(6)–C(7)–C(1)	130·2	H^2–C(11)–H^3	114
C(4)–C(10)–C(11)	111·0	H^1–C(12)–C(10)	111
C(4)–C(10)–C(12)	115·2	H^2–C(12)–C(10)	117
C(11)–C(10)–C(12)	109·4	H^3–C(12)–C(10)	113
H–C(3)–C(2)	107	H^1–C(12)–H^2	102
H–C(3)–C(4)	122	H^1–C(12)–H^3	112
H–C(5)–C(4)	115	H^2–C(12)–H^3	101
H–C(5)–C(6)	116		

The molecule may then be denoted by (IV) with partial π-electron delocalisation extending from O(9) round the ring to O(8) but not including, to any appreciable extent, the C(1)–C(2) bond. It cannot therefore be considered to be 'aromatic' in the accepted definition of the term,[1,2] and our results are accordingly in agreement with those of Bertelli and co-workers.[4] The electron delocalisation in 4-isopropyltropolone is intermediate in degree between that in 2-chlorotropone where it is smaller,[3] and in the tropolonate anion in sodium tropolonate [11] and in tropolonato-complexes of thorium(IV),[12] tin(IV),[13] and iron(III),[14] where apart from a long C(1)–C(2) bond, never substantially shorter than the single-bond value, the other C–C bonds assume lengths close to the aromatic value.

TABLE 4

Deviations of atoms from the least-squares plane through the seven-membered ring C(1)—(7) *

C(1)	−0·019 Å	O(8)	−0·036 Å
C(2)	−0·011	O(9)	−0·004
C(3)	0·021	C(10)	−0·024
C(4)	0·004	H[C(3)]	0·11
C(5)	−0·025	H[C(5)]	−0·01
C(6)	0·007	H[C(6)]	−0·05
C(7)	0·022	H[C(7)]	0·03

* Equation of plane: $14{\cdot}531x + 2{\cdot}556y + 5{\cdot}319z = 7{\cdot}402$ (where x, y, z are fractional co-ordinates).

The seven-membered ring deviates only slightly from planarity, the maximum deviation being 0·025 Å. Nevertheless, the deviations which are listed in Table 4 are highly significant (on four degrees of freedom $\chi^2 = 111{\cdot}1$). The hydroxy-oxygen atom is close to the mean plane through the ring but the carbonyl oxygen atom is displaced by 0·036 Å. The conformation of the isopropyl group is such that C(11) and C(12) lie on opposite sides of the mean plane through the ring at

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[7] D. W. J. Cruickshank, *Tetrahedron*, 1962, **17**, 155 and references therein.

[8] L. Pauling, 'The Nature of the Chemical Bond,' 3rd edn., Cornell University Press, Ithaca, New York, 1960.

[9] P. J. Wheatley, *J. Chem. Soc.*, 1964, 6036.

[10] D. J. Fries and M. Sundaralingam, *Acta Cryst.*, 1971, *B*, **27**, 401.

[11] Y. Sasada and I. Nitta, *Acta Cryst.*, 1956, **9**, 205; R. Shino, *ibid.*, 1961, **14**, 42.

[12] V. W. Day and J. L. Hoard, *J. Amer. Chem. Soc.*, 1970, **92**, 3626.

[13] J. J. Park, D. M. Collins, and J. L. Hoard, *J. Amer. Chem. Soc.*, 1970, **92**, 3636.

[14] T. A. Hamor and D. J. Watkin, *Chem. Comm.*, 1969, 440.

distances of 1·37 and 0·32 Å from it. The relevant torsion angles [15] are listed in Table 5. Torsion angles involving the hydrogen atoms of the methyl groups are generally close to 180 or ±60°.

TABLE 5

Torsion angles (deg.) for the isopropyl group

C(11)–C(10)–C(4)–C(3)	70·4
C(11)–C(10)–C(4)–C(5)	−107·8
C(12)–C(10)–C(4)–C(3)	−164·6
C(12)–C(10)–C(4)–C(5)	17·2
H[C(10)]–C(10)–C(4)–C(3)	−48
H[C(10)]–C(10)–C(4)–C(5)	134

Bond angles within the ring range from 122·8 to 131·1° (mean 128·55°). The smallest angle is at the carbonyl carbon atom and the general pattern of angle variation is similar to that found in the 2-chlorotropone structure. The two C–O bonds are slanted slightly towards one another which may be a manifestation of an attractive force between the negatively charged carbonyl oxygen atom and the positively charged hydroxy-oxygen atom [as depicted in formula (IV)].

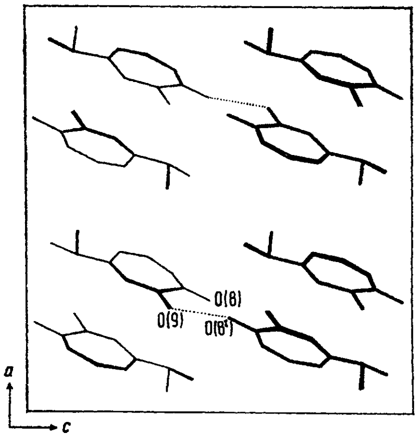

FIGURE 2 The crystal structure as viewed along the *b* axis

TABLE 6

The shorter intermolecular contacts (Å), excluding hydrogen atoms

O(9) ··· O(8^{I})	2·80	C(2) ··· C(4^{III})	3·69 Å
C(7) ··· O(9^{II})	3·42	C(10) ··· O(8^{III})	3·71
C(12) ··· O(8^{III})	3·42	C(4) ··· C(1^{III})	3·71
O(8) ··· O(8^{I})	3·45	C(1) ··· C(10^{III})	3·72
O(8) ··· C(7^{I})	3·51	C(5) ··· O(9^{III})	3·74
C(6) ··· O(9^{II})	3·52	C(3) ··· C(6^{III})	3·77
C(2) ··· C(5^{III})	3·68		

The superscripts refer to molecules in the following equivalent positions relative to the reference molecule at *x*, *y*, *z*:

I $\frac{1}{2} - x, \frac{1}{2} + y, 1 - z$ II $x, -1 + y, z$
III $\frac{1}{2} - x, \frac{1}{2} - y, \frac{1}{2} - z$

The arrangement of the molecules in the unit cell as viewed along the *b* axis is illustrated in Figure 2. Intermolecular contact distances of <3·8 Å involving the heavier atoms are listed in Table 6. Hydrogen bonding appears to be involved in the O(9) ··· O(8^{I}) contact of 2·80 Å which links the molecules in chains parallel to the *b* axis. The donor angle C(2)–O(9) ··· O(8^{I}) is 140·7°. Unfortunately the pertinent hydrogen atom could not be located (see Experimental section). All other contacts correspond to normal van der Waals interactions.

EXPERIMENTAL

Crystal Data.—$C_{10}H_{12}O_2$, $M = 164·2$, Monoclinic, $a = 17·063$, $b = 6·469$, $c = 15·970$ Å, $\beta = 90·77°$, $U = 1762·6$ Å^3, $D_m = 1·21$, $Z = 8$, $D_c = 1·24$, $F(000) = 704$. Systematic absences: *hkl* when $h + k + l$ is odd, *h0l* when *l* is odd, establish space group *Ic* or *I*2/*c*; shown to be *I*2/*c* (C_{2h}^{6}) as a result of this analysis.* Cu-K_α radiation, $\lambda = 1·5418$ Å; μ(Cu-K_α) = 7·0 cm^{-1}.

Crystallographic Measurements.—Crystals (Koch–Light) were cut to give cubes of edge 0·25 mm. The space group and approximate cell dimensions were obtained from oscillation and Weissenberg photographs. The final cell dimensions and intensity data were measured with a Hilger and Watts four-circle automatic diffractometer by use of nickel-filtered Cu-K_α radiation and a scintillation counter. From 1695 reflections scanned within the range $2\theta \leq 140°$, 1272, for which the net intensity was $>3\sigma$ from counting statistics, were considered to be observed and were used in the structure analysis. The ω scan mode was employed, and for each reflection fifty 2 s counts at intervals of 0·02° were taken. Peak and background intensities were obtained by an ordinate analysis procedure described by Watson.[16] No absorption corrections were applied in converting the intensities to structure amplitudes.

Structure Analysis. The phases of the 214 largest *E* values (>1·6) were determined by the symbolic addition procedure [17] using the program CSSA of Hodder, Prout, and Rollett. The *E* map calculated with these phases revealed the positions of all the atoms of the molecule (apart from hydrogen atoms). At this stage *R* was 24·5% and one cycle of isotropic least-squares refinement followed by a cycle in which the atoms were allowed to vibrate anisotropically reduced *R* to 12·8%. A Fourier difference synthesis was now computed and from this all the hydrogen atoms were located, except that linked to the hydroxy-oxygen O(9). The hydrogen atoms which had been located were included in the calculations with isotropic temperature factors but only their co-ordinates were refined. The least-squares calculations were terminated when the calculated shifts for the non-hydrogen atom parameters were all $<0·1\sigma$. The final value of *R* is 8·3% for 1272 structure amplitudes.†

The weighting scheme used in the final cycles of refinement was: $w^{\frac{1}{2}} = 1·0$ if $|F_o| \leq 8·5$, $w^{\frac{1}{2}} = 8·5/|F_o|$ if $8·5 < |F_o| \leq 23·5$, and $w^{\frac{1}{2}} = 0·36$ if $|F_o| > 23·5$.

Atomic scattering factors for carbon and oxygen were taken from ref. 18 and those for hydrogen from ref. 19.

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* Equivalent positions for this non-standard orientation are: $(0,0,0;\ \frac{1}{2},\frac{1}{2},\frac{1}{2}) \pm (x, y, z;\ x, -y, \frac{1}{2} + z)$.

† Observed and calculated structure factors are published in Supplementary Publication No. SUP 20317 (10 pp., 1 microfiche). Details of Supplementary Publications are in Notice to Authors No. 7, *J. Chem. Soc.* (*A*), 1970, Issue No. 20.

[15] E. L. Eliel, N. L. Allinger, S. J. Angyal, and G. A. Morrison, 'Conformational Analysis,' Interscience, New York, 1965.

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