# Crystal Structure of the Tricyclic Diterpene Derivative 18-Hydroxydecipia-2(4),14-dien-1-oic Acid

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The crystal structure of the title compound, a new tricyclic diterpene derivative extracted from *Eremophila decipiens* containing the tricyclo[5.3.1.$0^{5,11}$]undecane ring system, has been determined by *X*-ray diffraction from diffractometer data and refined by least squares to *R* 0.062 for 1 065 reflections with $I > 3\sigma(I)$. Crystals of the derivative, $C_{20}H_{30}O_3$, are orthorhombic, space group $P2_12_12_1$, $a$ = 36.95(2), $b$ = 7.467(5), $c$ = 6.676(5) Å, $Z$ = 4.

THIS paper describes the elucidation by *X*-ray crystallography of the crystal and molecular structure of a new tricyclic terpene derivative extracted from the Australian plant *Eremophila decipiens*, together with a number of related compounds, whose chemistry has been described elsewhere.[1] Crystals of the substance were obtained as long fragile plates from n-pentane solution. A crystal 0.05 × 0.30 × 0.80 mm was used.

## EXPERIMENTAL

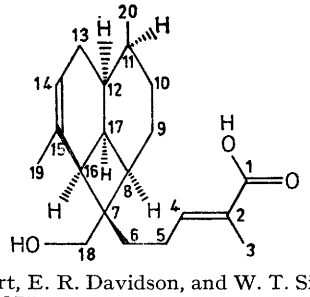
Unit-cell calibration was carried out by a least-squares fit of the angular parameters of 15 reflections with $2\theta \sim 30°$ centred in the counter aperture of a Syntex $P\bar{1}$ four-circle diffractometer. A unique data set in the range $2\theta < 100°$ was gathered by a conventional $2\theta$—$\theta$ scan, yielding 1 158 independent reflections, 1 065 of which with $I > 3\sigma(I)$ were used in the structure solution and refinement after correction for absorption.

*Crystal Data.*—$C_{20}H_{30}O_3$, $M$ = 318.5. Orthorhombic, space group $P\ 2_12_12_1$ ($D_2^4$, No. 19), $a$ = 36.95(2), $b$ = 7.467(5), $c$ = 6.676(5) Å, $U$ = 1 842(2) Å$^3$, $D_m$ = 1.15(1), $Z$ = 4, $D_c$ = 1.148 g cm$^{-3}$, $F(000)$ = 728, Cu-$K_\alpha$ radiation, (Ni filtered), $\lambda$ = 1.5418 Å; $\mu$(Cu-$K_\alpha$) = 5.20 cm$^{-1}$. Neutral-atom scattering factors [2,3] (no correction for anomalous dispersion).

Solution of the structure by tangent refinement yielded a complete molecular skeleton. Refinement of the structure was carried out by 9 × 9 block-diagonal least-squares. In the final stages, the parameters of the molecular skeleton were refined as two blocks comprising the 'tail' of the molecule and the core, the parameters of the hydrogen atoms being refined as a third block; anisotropic thermal parameters of the form exp $[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$ were used for the non-hydrogen atoms, while the latter were refined with the corresponding isotropic parameters fixed at 0.10 Å$^2$. At convergence, parameter shifts were $< 0.2\sigma$, $R$ was 0.062, and $R'$ 0.090 $[R' = (\Sigma w||F_o| - |F_c||^2/\Sigma w|F_o|^2)^{\frac{1}{2}}]$; the appropriate weighting scheme was of the form $w = [\sigma^2(F_o)^2 + n \times 10^{-4}(F_o)^2]^{-1}$, requiring $n$ = 4.

Computation was carried out on the local CDC 6 200 machine using a local variant of the *X*-Ray '72 program system.[4] Structure-factor tables and non-hydrogen atom torsion angles are deposited as Supplementary Publication No. SUP 21492 (9 pp., 1 microfiche).† Atomic positional and thermal parameters are listed in Table 1.

Atomic labelling is as follows for the non-hydrogen skeleton:




† For details, see Notice to Authors, No. 7, *J.C.S. Perkin II*, 1975, Index issue.

[1] E. L. Ghisalberti, P. R. Jefferies, and P. N. Sheppard, *Tetrahedron Letters*, 1975, 1775.

[2] R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, 1965, **42**, 3175.

[3] D. T. Cromer and J. B. Mann, *Acta Cryst.*, 1968, *A***24**, 321.

[4] '*X*-Ray' System, Technical Report TR 192, Computer Science Centre, University of Maryland, U.S.A., June, 1972.

TABLE 1

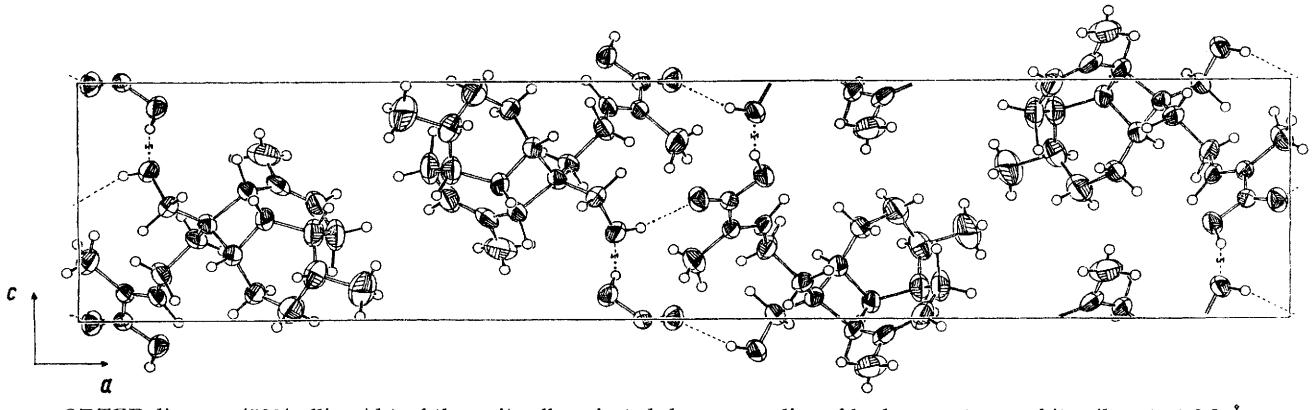
Atomic positional ($x,y,z$) and thermal parameters ($\times 10^3$ Å$^2$), with least-squares estimated standard deviations in final digit in parentheses

(*a*) Non-hydrogen atoms

| Atom | $10^4x$ | $10^4y$ | $10^4z$ | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{12}$ | $U_{13}$ | $U_{23}$ |
|---|---|---|---|---|---|---|---|---|---|
| C(1) | 4 639(2) | 9 992(9) | −0 321(10) | 34(4) | 35(4) | 51(4) | −1(4) | −3(3) | 7(4) |
| C(2) | 4 623(2) | 8 812(9) | 1 445(11) | 33(3) | 37(4) | 64(5) | −3(3) | −10(4) | 16(4) |
| C(3) | 4 932(2) | 7 477(10) | 1 600(13) | 51(4) | 69(6) | 110(7) | 14(4) | −2(5) | 26(6) |
| C(4) | 4 362(2) | 8 967(9) | 2 745(10) | 33(4) | 42(4) | 59(4) | −11(3) | 1(4) | 14(4) |
| C(5) | 4 329(2) | 8 024(9) | 4 753(11) | 41(4) | 58(5) | 68(5) | −14(4) | −4(4) | 16(5) |
| C(6) | 4 036(2) | 6 539(9) | 4 700(11) | 45(4) | 41(4) | 63(5) | −6(3) | −1(3) | 15(4) |
| C(7) | 3 940(2) | 5 908(8) | 6 824(9) | 36(3) | 41(4) | 43(4) | −6(3) | 1(3) | 16(4) |
| C(8) | 3 739(2) | 7 239(8) | 8 222(11) | 36(3) | 46(4) | 63(5) | 1(3) | 0(4) | 9(4) |
| C(9) | 3 554(2) | 8 854(9) | 7 364(12) | 41(4) | 48(4) | 88(6) | 6(3) | 12(4) | 21(5) |
| C(10) | 3 260(2) | 9 547(11) | 8 819(13) | 66(5) | 75(6) | 87(6) | 13(5) | 7(5) | 1(6) |
| C(11) | 3 059(2) | 8 065(12) | 9 951(12) | 56(4) | 84(6) | 74(6) | 15(5) | 17(4) | −7(6) |
| C(12) | 3 066(2) | 6 303(12) | 8 824(13) | 40(4) | 81(6) | 87(6) | 4(4) | 9(4) | 20(6) |
| C(13) | 2 891(2) | 6 385(14) | 6 740(14) | 35(4) | 101(7) | 98(7) | −1(5) | −8(4) | 10(7) |
| C(14) | 3 040(2) | 5 128(13) | 5 216(15) | 52(5) | 81(6) | 104(7) | −21(5) | −16(5) | 14(7) |
| C(15) | 3 359(2) | 4 304(9) | 5 336(13) | 55(5) | 43(4) | 87(6) | −22(4) | −5(4) | 9(5) |
| C(16) | 3 609(2) | 4 543(8) | 7 053(11) | 37(3) | 41(4) | 79(5) | −8(3) | −2(3) | 18(4) |
| C(17) | 3 467(2) | 5 713(10) | 8 806(13) | 34(3) | 53(4) | 91(6) | 1(3) | 14(4) | 18(5) |
| C(18) | 4 262(2) | 5 179(9) | 7 965(11) | 39(3) | 44(4) | 70(5) | 9(3) | 2(4) | 4(4) |
| C(19) | 3 473(2) | 3 007(11) | 3 743(14) | 107(6) | 51(5) | 101(7) | −14(5) | −22(6) | 6(6) |
| C(20) | 2 674(2) | 8 678(14) | 10 517(18) | 79(6) | 128(8) | 137(9) | 26(6) | 48(7) | −11(9) |
| O(0) | 4 893(1) | 10 058(6) | −1 495(7) | 42(2) | 63(3) | 60(3) | 5(3) | 15(2) | 12(3) |
| O(1) | 4 353(1) | 11 021(6) | −0 604(7) | 41(3) | 53(3) | 80(4) | 8(2) | 11(3) | 31(3) |
| O(18) | 4 422(1) | 3 683(6) | 6 938(7) | 42(2) | 48(3) | 69(3) | 8(2) | 12(2) | 8(3) |

(*b*) Hydrogen atoms

| Atom | $10^3x$ | $10^3y$ | $10^3z$ | Atom | $10^3x$ | $10^3y$ | $10^3z$ |
|---|---|---|---|---|---|---|---|
| H(1) | 442(2) | 1 187(11) | −150(12) | H(12α) | 295(2) | 526(11) | 986(12) |
| H(3a) | 510(2) | 795(10) | 198(13) | H(13α) | 263(2) | 604(10) | 666(13) |
| H(3b) | 502(2) | 674(11) | 036(12) | H(13β) | 292(2) | 795(11) | 582(13) |
| H(3c) | 487(2) | 637(11) | 267(14) | H(14) | 288(2) | 466(11) | 410(12) |
| H(4) | 419(2) | 1 006(11) | 274(11) | H(16α) | 369(2) | 320(11) | 716(13) |
| H(5a) | 454(2) | 747(10) | 510(13) | H(17α) | 356(2) | 494(11) | 1 018(12) |
| H(5b) | 422(2) | 914(11) | 593(12) | H(18) | 463(2) | 389(10) | 634(12) |
| H(6a) | 382(2) | 704(11) | 390(13) | H(18a) | 447(2) | 617(11) | 824(12) |
| H(6b) | 415(2) | 559(11) | 397(11) | H(18b) | 415(2) | 478(11) | 962(12) |
| H(8α) | 391(2) | 772(11) | 954(13) | H(19a) | 329(2) | 305(10) | 246(12) |
| H(9α) | 373(2) | 970(10) | 692(13) | H(19b) | 372(2) | 320(12) | 316(12) |
| H(9β) | 343(2) | 872(11) | 609(12) | H(19c) | 350(2) | 213(11) | 420(13) |
| H(10α) | 338(2) | 1 026(11) | 985(12) | H(20a) | 270(2) | 985(11) | 1 139(12) |
| H(10β) | 307(2) | 1 004(10) | 789(12) | H(20b) | 256(2) | 769(11) | 1 096(14) |
| H(11α) | 321(2) | 818(11) | 1 110(11) | H(20c) | 255(2) | 895(11) | 940(14) |




ORTEP diagram (50% ellipsoids) of the unit cell projected down $c$; radius of hydrogen atoms arbitrarily set at 0.1 Å

With the exception of O(0), oxygen atoms are labelled according to the carbon atom they are attached to. Hydrogen atoms are labelled similarly followed by α or β depending on the configuration, or a, b, c, where configuration is irrelevant. The carbon skeleton of this compound is assigned the trivial name decipiane.

## DISCUSSION

The unit cell (Figure) comprises discrete molecules of the compound $C_{22}H_{30}O_3$; the chief intermolecular interactions are hydrogen bonds from the carboxy-group *via* the hydrogen atom H(1) to the hydroxylic oxygen, and

TABLE 2

Interatomic distances (Å) and angles (deg), with least-squares estimated standard deviations in parentheses

| | |
|---|---|
| C(1)–O(0) | 1.225(8) |
| C(1)–O(1) | 1.320(7) |
| O(1)–H(1) | 0.91(8) |
| C(1)–C(2) | 1.473(9) |
| C(2)–C(3) | 1.519(9) |
| C(2)–C(4) | 1.304(9) |
| C(3)–H(3a) | 0.76(8) |
| C(3)–H(3b) | 1.04(8) |
| C(3)–H(3c) | 1.12(8) |
| C(4)–H(4) | 1.04(8) |
| C(4)–C(5) | 1.518(10) |
| C(5)–H(5a) | 0.90(8) |
| C(5)–H(5b) | 1.22(8) |
| C(5)–C(6) | 1.551(9) |
| C(6)–H(6a) | 1.03(8) |
| C(6)–H(6b) | 0.96(8) |
| C(6)–C(7) | 1.536(9) |
| C(7)–C(8) | 1.553(9) |
| C(7)–C(16) | 1.600(8) |
| C(7)–C(18) | 1.513(9) |
| C(8)–C(9) | 1.499(9) |
| C(8)–H(8α) | 1.14(8) |
| C(8)–C(17) | 1.569(9) |
| C(9)–C(10) | 1.546(11) |
| C(9)–H(9α) | 0.96(8) |
| C(9)–H(9β) | 0.97(8) |
| C(10)–C(11) | 1.533(12) |
| C(10)–H(10α) | 0.97(8) |
| C(10)–H(10β) | 1.00(8) |
| C(11)–C(12) | 1.516(13) |
| C(11)–C(20) | 1.539(12) |
| C(11)–H(11α) | 0.95(7) |
| C(20)–H(20a) | 1.05(8) |
| C(20)–H(20b) | 0.91(8) |
| C(20)–H(20c) | 0.90(9) |
| C(12)–C(13) | 1.535(13) |
| C(12)–C(17) | 1.546(9) |
| C(12)–H(12α) | 1.13(8) |
| C(13)–C(14) | 1.490(13) |
| C(13)–H(13α) | 0.99(7) |
| C(13)–H(13β) | 1.33(8) |
| C(14)–C(15) | 1.333(11) |
| C(14)–H(14) | 1.00(8) |
| C(15)–C(16) | 1.483(11) |
| C(15)–C(19) | 1.500(12) |
| C(19)–H(19a) | 1.09(8) |
| C(19)–H(19b) | 0.99(8) |
| C(19)–H(19c) | 0.73(8) |
| C(16)–C(17) | 1.553(10) |
| C(16)–H(16α) | 1.05(9) |
| C(18)–O(18) | 1.439(8) |
| C(18)–H(18a) | 1.08(8) |
| C(18)–H(18b) | 1.22(8) |
| O(18)–H(18) | 0.87(7) |
| C(17)–H(17α) | 1.13(8) |
| | |
| C(12)–C(13)–C(14) | 116.0(7) |
| C(12)–C(13)–H(13α) | 116(5) |
| C(12)–C(13)–H(13β) | 115(4) |
| C(14)–C(13)–H(13α) | 99(5) |
| C(14)–C(13)–H(13β) | 102(4) |
| H(13α)–C(13)–H(13β) | 107(6) |
| C(13)–C(14)–C(15) | 125.2(8) |
| C(13)–C(14)–H(14) | 121(4) |
| C(15)–C(14)–H(14) | 113(5) |
| C(14)–C(15)–C(16) | 122.8(8) |
| C(14)–C(15)–C(19) | 120.3(8) |
| C(16)–C(15)–C(19) | 116.8(6) |
| C(15)–C(19)–H(19a) | 111(4) |
| C(15)–C(19)–H(19b) | 116(5) |
| C(15)–C(19)–H(19c) | 109(7) |
| H(19a)–C(19)–H(19b) | 105(6) |
| H(19a)–C(19)–H(19c) | 117(8) |
| H(19b)–C(19)–H(19c) | 98(8) |
| C(15)–C(16)–C(7) | 118.6(6) |
| C(17)–C(16)–C(7) | 88.4(5) |

TABLE 2 (*Continued*)

| | |
|---|---|
| C(15)–C(16)–C(17) | 116.0(5) |
| C(7)–C(16)–H(16α) | 113(4) |
| C(17)–C(16)–H(16α) | 126(5) |
| C(15)–C(16)–H(16α) | 97(4) |
| C(18)–O(18)–H(18) | 116(5) |
| C(1)–O(1)–H(1) | 106(5) |
| O(1)–C(1)–O(0) | 119.9(6) |
| O(1)–C(1)–C(2) | 115.6(5) |
| O(0)–C(1)–C(2) | 124.5(6) |
| C(1)–C(2)–C(3) | 114.7(6) |
| C(1)–C(2)–C(4) | 120.6(6) |
| C(3)–C(2)–C(4) | 124.7(7) |
| H(3a)–C(3)–C(2) | 109(6) |
| H(3b)–C(3)–C(2) | 121(4) |
| H(3c)–C(3)–C(2) | 112(4) |
| H(3a)–C(3)–H(3b) | 106(7) |
| H(3a)–C(3)–H(3c) | 107(7) |
| H(3b)–C(3)–H(3c) | 100(6) |
| C(2)–C(4)–H(4) | 122(4) |
| C(2)–C(4)–C(5) | 127.3(6) |
| H(4)–C(4)–C(5) | 109(4) |
| C(4)–C(5)–C(6) | 111.5(6) |
| C(4)–C(5)–H(5a) | 112(5) |
| C(4)–C(5)–H(5b) | 106(4) |
| H(5a)–C(5)–H(5b) | 116.5(6) |
| H(5a)–C(5)–C(6) | 106(5) |
| H(5b)–C(5)–C(6) | 105(4) |
| C(5)–C(6)–C(7) | 111.0(6) |
| C(5)–C(6)–H(6a) | 107(4) |
| C(5)–C(6)–H(6b) | 103(5) |
| H(6a)–C(6)–H(6b) | 111(7) |
| H(6a)–C(6)–C(7) | 114(5) |
| H(6b)–C(6)–C(7) | 110(5) |
| C(6)–C(7)–C(8) | 118.0(5) |
| C(6)–C(7)–C(16) | 117.3(5) |
| C(6)–C(7)–C(18) | 113.3(5) |
| C(8)–C(7)–C(16) | 89.1(4) |
| C(8)–C(7)–C(18) | 107.7(5) |
| C(16)–C(7)–C(18) | 108.9(5) |
| C(7)–C(8)–C(9) | 120.2(6) |
| C(7)–C(8)–C(17) | 89.5(5) |
| C(7)–C(8)–H(8α) | 114(4) |
| C(9)–C(8)–C(17) | 112.7(5) |
| C(9)–C(8)–H(8α) | 107(4) |
| C(17)–C(8)–H(8α) | 113(4) |
| C(8)–C(9)–C(10) | 110.4(6) |
| C(8)–C(9)–H(9α) | 109(5) |
| C(8)–C(9)–H(9β) | 118(5) |
| H(9α)–C(9)–H(9β) | 97(7) |
| C(10)–C(9)–H(9α) | 117(5) |
| C(10)–C(9)–H(9β) | 105(5) |
| C(9)–C(10)–C(11) | 114.2(7) |
| C(9)–C(10)–H(10α) | 109(5) |
| C(9)–C(10)–H(10β) | 103(5) |
| C(11)–C(10)–H(10α) | 105(5) |
| C(11)–C(10)–H(10β) | 104(5) |
| H(10α)–C(10)–H(10β) | 123(7) |
| C(10)–C(11)–C(12) | 111.9(7) |
| C(10)–C(11)–C(20) | 110.8(7) |
| C(10)–C(11)–H(11α) | 93(5) |
| C(12)–C(11)–C(20) | 113.3(7) |
| C(12)–C(11)–H(11α) | 118(5) |
| C(20)–C(11)–H(11α) | 108(5) |
| C(11)–C(20)–H(20a) | 108(4) |
| C(11)–C(20)–H(20b) | 106(5) |
| C(11)–C(20)–H(20c) | 110(5) |
| H(20a)–C(20)–H(20b) | 122(7) |
| H(20a)–C(20)–H(20c) | 108(7) |
| H(20b)–C(20)–H(20c) | 102(7) |
| C(11)–C(12)–C(13) | 114.1(7) |
| C(11)–C(12)–C(17) | 105.5(6) |
| C(11)–C(12)–H(12α) | 107(4) |
| C(13)–C(12)–C(17) | 114.0(7) |
| C(13)–C(12)–H(12α) | 115(4) |
| C(17)–C(12)–H(12α) | 101(4) |
| C(12)–C(17)–H(17α) | 115(4) |
| C(12)–C(17)–C(8) | 114.2(6) |
| C(12)–C(17)–C(16) | 119.4(6) |
| C(8)–C(17)–C(16) | 90.2(5) |

TABLE 2 (*Continued*)

| | |
|---|---|
| C(16)–C(17)–H(17α) | 103(4) |
| C(8)–C(17)–H(17α) | 112(4) |
| C(7)–C(18)–O(18) | 111.3(5) |
| C(7)–C(18)–H(18a) | 113(4) |
| C(7)–C(18)–H(18b) | 105(4) |
| O(18)–C(18)–H(18a) | 109(4) |
| O(18)–C(18)–H(18b) | 113(4) |
| H(18a)–C(18)–H(18b) | 105(6) |
| | |
| H(1) · · · O(18$^{I}$) | 1.71(8) |
| H(18) · · · O(0$^{II}$) | 1.98(7) |
| O(1)–H(1) · · · O(18) | 162(7) |
| O(18)–H(18) · · · O(0) | 146(7) |

Transformations of the asymmetric unit *x*, *y*, *z*:
I *x*, 1 + *y*, *z* − 1 II 1 − *x*, *y* − ½, ½ − *z*

*via* the carbonyl oxygen to the hydroxylic hydrogen (Table 2); other contacts are greater than the van der Waal's distances.

The structure determination definitively establishes the following points which provide necessary confirmation for the chemical studies. (*a*) The nature and stereochemistry of the ring system is based on the tricyclo[5.3.1.0 $^{5,11}$]undecane skeleton. Five of the six chiral centres in the ring system have hydrogen atoms all of which are α [H(8), H(11), H(12), H(16) and H(17)]; at the remaining centre at C(7), the $CH_2OH$ group is *cis* to the α hydrogens H(8), H(16) and H(17). (*b*) The stereochemistry of the double bond in the side-chain is established to be *E* or *trans*.

The following features arise from the nature of the ring fusion: (i) the cyclobutane ring, as usual, is considerably distorted from planarity (Table 3); (ii) the cyclohexene ring is distorted to a non-classical configuration with C(12) and C(17) being on the same side of plane (iii) (Table 3); and (iii) the torsion angles H(11α)–C(11)–C(10)–H(10α) and H(11α)–C(11)–C(10)–H(10β) are respectively −21.9 and −151.9°, indicating that the ring C(8)—(12), C(17) which forms an approximate boat with C(9) and C(12) as apices is considerably twisted.

Deviations of the double bond systems O(0), O(1), C(1)—(5) and C(13)—16, C(19) from planarity, although

TABLE 3

Least-squares planes in the form $pX + qY + rZ = s$, where the orthogonal Å frame is defined by $X = ax$, $Y = by$, $Z = cz$. σ Å is the estimated standard deviation of the defining atoms; and atom deviations (Å) are in square brackets

| $10^4p$ | $10^4q$ | $10^4r$ | $s$ | σ | $\chi^2$ |
|---|---|---|---|---|---|
| Plane (i): O(0), O(1), C(1)—(5), H(4) | | | | | |
| 5 425 | 6 807 | 4 922 | 14.27 | 0.10 | 89.7 |
| [O(1) −0.14, O(0) 0.16, C(1) 0.00, C(2) −0.05, C(3) −0.06, C(4) −0.07, C(5) 0.04, C(6) −1.32, H(4) 0.13] | | | | | |
| Plane (ii): C(7), C(8), C(16), C(17) | | | | | |
| 5 705 | −4 121 | 7 104 | 9.64 | 0.10 | 381 |
| [C(7) 0.08, C(8) −0.08, C(16) −0.08, C(17) 0.08, C(15) −1.35, C(12) −0.93, C(9) −1.38, C(6) −0.92, C(18) 1.53] | | | | | |
| Plane (iii): C(13)—(16), C(19), H(14) | | | | | |
| 4 105 | 7 544 | −5 122 | 5.664 | 0.05 | 9.22 |
| [C(13) 0.01, C(14) 0.05, C(15) 0.03, C(16) −0.04, C(19) 0.02, C(12) −0.48, C(17) −0.20, C(7) 1.31, C(8) 1.27, C(11) 0.11, H(14) −0.07] | | | | | |

significant are minor; bond lengths and angles throughout the system are unremarkable.

As a result of the ring fusion, a number of close intramolecular non-bonding hydrogen-hydrogen approaches < 2.5 Å are found between non-adjacent carbon atoms; these are H(6a) · · · H(9β) 2.4(1), H(6b) · · · H(19b) 2.5(1), and H(13β) · · · H(10β) 2.2(1) Å.

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